Metals in the Admittance Diagram

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Introduction
We have described the admittance diagram in two previous articles [1, 2]. We now extend the diagram to deal with metals. This paper is essentially a continuation of [2]. We use the nomenclature and symbols already defined there.

We recall that the admittance diagram is one of a family of graphical techniques that are of interest in explaining, rather than calculating, performance of a thin-film coating. We use the computer for calculation, but the computer is not good at assessing either feasibility or correctness, or conveying an understanding. We use other techniques for these purposes, the admittance diagram being one of them.

The admittance diagram shows the locus, in the complex plane, of the variation of surface admittance through the coating, starting at the rear, or exit, surface and terminating at the front, or incident, surface. The locus is continuous, and, for dielectric materials, consists of a series of connected arcs of circles, centered on the real axis and described clockwise. Metal loci are a little more difficult.

Fortunately, metals of high optical performance have large k and small n. This leads to the idea of a perfect metal that has finite k and zero n. Once we understand the behavior of a perfect metal, the extension to one that is imperfect is straightforward.

Metals at Normal Incidence
Thin films are described by a characteristic admittance, y, and a phase thickness, δ, given by:

\[ y = (n - ik) \]
\[ \delta = \frac{2\pi(n - ik)d}{\lambda} \]  \hspace{1cm} (1)

where y is in free space units. For a perfect metal this becomes:

\[ y = -ik \]
\[ \delta = -i\beta = -\frac{2\pi kd}{\lambda} \]  \hspace{1cm} (2)

In this perfect metal there is no phase change associated with propagation of the wave, simply an exponential decay with distance. Thus it is better to use β than phase thickness δ to characterize the metal film. When these parameters are entered in the usual matrix expression, the circular functions become hyperbolic. Otherwise, the matrices are quite similar in their behavior to those for dielectric thin films. In particular, the admittance locus of a perfect metal is circular, centered on the real axis and described clockwise with increasing thickness. Of course there is now no quarterwave rule, but the circles cut the real axis in two points a and b related by

\[ ab = -k^2 \]  \hspace{1cm} (3)

This implies that a and b are on opposite sides of the imaginary axis. Now, instead of a nested set of circles, we have an intersecting set, and it can be shown that there are just two points of intersection for the entire set. These points are at k and -k on the imaginary axis. The region containing the negative limb of the real axis is inaccessible (unless there is gain in the system) and so the loci are circular and start at k and terminate at -k on the imaginary axis. Contours of constant β are two nested sets of circles centered on the imaginary axis and nested about the points k and -k on it. Figure 1 shows the arrangement. Of course, if the locus starts on the imaginary axis at any point other than k, then the locus will remain on the imaginary axis.

Real metals have nonzero n. In metals we class as high performance, like silver, the value of n is quite small in the spectral region where we would use the metal in an interference role, usually the visible and very near infrared. When n is small the diagram changes slightly. It is as if we seized the arrangement in Figure 1 and twisted it around the origin so that the points k and -k on the imaginary axis move to the points (-n,k) and (n,-k) respectively. Figure 2 illustrates this. Now the termination point for all the loci is the admittance of the metal, n-ik, as would be expected. The small excursion into the region on the left-hand side of the imaginary axis, is, of course, into the forbidden region and is shown just for reference. There are also some residual short loci shown on the other side of the termination point, joining the imaginary axis to it. These are reversed in direction, that is, they move from the imaginary axis to the termination point.

Figure 3 shows a calculated set of loci for silver at 510nm where the optical constants are taken as 0.051–i2.96. The loci are virtually perfect circles and quite similar to Figure 2.

Although β is a useful quantity to characterize the optical thickness of the metal, it is not as powerful as δ for dielectrics. The contours of constant β are difficult to relate to a particular value of β. We can say with certainty, however, that the gap between two particular contours represents the same change in β, regardless of the particular locus that is being followed.

More heavily absorbing metals tend to have large n as well as large k. In such cases the circles degenerate into spirals that terminate at the value of the optical constants. Figure 4 is a typical example showing chromium loci at 510nm where the optical constants are 2.86-13.32.

The extinction coefficient, k, of metals is usually roughly proportional to wavelength λ. Thus, as the wavelength increases, the points k and -k on the imaginary axis move away from the origin. The contours of constant β expand. The change in β associated with the thickness of a metal layer remains roughly constant, because k/λ is constant. Thus the
locus associated with any metal layer tends to lengthen as wavelength increases. This is the opposite of the behavior of a dielectric layer, where the locus shortens because \( n \) remains roughly constant and \( \delta \) shrinks. Thus, with increasing wavelength, metals become stronger in their effects, while dielectrics weaken.

Figure 1 to Figure 3 show immediately why it is that multilayers made entirely of metals are rather uninteresting. It matters little which metal is involved. All move towards their termination points that are located in the lower part of the admittance diagram, usually close to the imaginary axis. This implies that a metal multilayer exhibits a behavior that is quite similar to that for a single metal layer. As the thickness increases, the reflectance increases. To move around the admittance diagram at will, it is necessary to employ dielectrics. Thus the interesting interference coatings are either all-dielectric or metal-dielectric. Of course we use metal multilayers in the soft x-ray region, but there, the metals are operating beyond their plasma frequencies, and so present properties much more like dielectrics.

Although metals absorb, the high performance metals can have significant transmittance, and so they are used in transmitting coatings especially bandpass and heat reflecting filters. In these applications they present the advantage that their increasing strength with wavelength helps in rejecting the infrared. We discussed the electric field distribution in the earlier paper, [2], where it was shown that the electric field at a point in a coating is higher the nearer the point is to the imaginary axis. Although the absorption loss in a metal layer means that this rule is no longer completely accurate, nevertheless it is still a good approximation when the metal is of high performance, that is low \( n \). This explains why a dielectric-metal-dielectric construction is superior to a metal-dielectric-metal. Figure 5 represents an extreme case where we compare a three-layer metal-dielectric-metal filter, based on silver, with an induced transmission filter consisting of 19 layers, two of which are silver. The two metal layers in the metal-dielectric-metal filter are of thicknesses 61.6nm and 40nm, while the layers in the induced transmission filter are both of thickness 61.6nm. The difference in peak transmittance is considerable and can be explained by the much lower electric field designed into the metal layers of the induced transmission filter. Figure 6 shows the important parts of the admittance loci. The entire three layers of the metal-dielectric-metal are shown, but, for clarity, only the central five layers of the induced transmission filter. The metal layers are the important ones and they are labeled in the figure. The two silver layers of the induced transmission filter are over to the right of those in the metal-dielectric-metal. Hence they experience a rather lower electric field with lower accompanying loss. In fact, the induced transmission filter design procedure [3, 4] finds the optimum loci for the metal layers. We can not do better.

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\[ \eta_p = \frac{y \cos \theta_p}{\cos \theta} \]

\[ \eta_s = \frac{y \cos \theta_s}{\cos \theta} \]

\( \theta \) being the angle in the appropriate material. This works well for dielectric materials but there is a problem when we turn to metals because of the complex optical properties. Snell’s Law becomes:

\[ \eta_p = \frac{\eta \cos \theta_p}{\cos \theta} \]

and \( \theta \) is now complex. Fortunately, we do not actually need \( \theta \). The expression we want is \((n-ik)\cos\theta\) and it is possible to derive this without having to worry about the implications of a complex angle. From equation 4,

\[ \eta_p \cos \theta_p = (n-ik) \sqrt{1 - \sin^2 \theta} \]

\[ = \sqrt{n^2 - k^2 - n_0^2 \sin^2 \theta_0 - i2nk} \]

There are two roots, one in the second quadrant and one in the fourth. Physical considerations tell us that the fourth quadrant solution is correct. Then we have:

\[ \eta_p = \frac{n^2 - k^2 - n_0^2 \sin^2 \theta_0 - i2nk}{\cos \theta_0} \]

and

\[ \eta_s = \frac{(n-ik)^2}{\eta_p} \]

the quadrant of \( \eta_p \) being unambiguously assigned by the expression . Note that these expressions apply to any material, whatever its level of absorption.

Although we will not make much use of it in this article, equation leads to the expression we need for \( \delta \), the phase thickness of the layer:

\[ \delta = \frac{2\pi d}{\lambda} \sqrt{n^2 - k^2 - n_0^2 \sin^2 \theta_0 - i2nk} \]

the fourth quadrant root being the correct one.

The high-performance metals have rather large \( k \). The square of \( k \) is much larger than the square of \( n_0 \sin \theta_0 \), that is usually rather less than unity. For the high-performance metals, therefore, we can write approximately:

\[ \eta_s = \frac{n-ik}{\cos \theta_0} \]  
\[ \eta_p = (n-ik) \cos \theta_0 \]

This simplification has sometimes prompted the mistaken view that metal coatings do not suffer from a sensitivity to polarization.

Let us examine a metal like silver, or aluminum, used as a front surface mirror and let us vary the angle of incidence. The metal can be considered thick enough to be opaque, when we can think of the metal as the substrate, and we have to consider only the metal-incident medium interface. Let the metal have optical constants \( n-ik \) so that expresses the variation of admittance with angle. Figure 7 illustrates the behavior. For the sake of clarity we have exaggerated the value of \( n \) so that the red line joining the origin to the point \( n-ik \) is tilted at a reasonable angle to the imaginary axis. We imagine that \( k \) is numerically greater than \( n_0 \).

At normal incidence both admittances coincide at \( n-ik \). Then, as the angle of incidence increases, the \( p \) and \( s \)-admittances move along the red line, \( p \) towards the origin. The reflectance for \( p \)-polarization falls while that for \( s \)-polarization rises. The reflectance phase change, \( \phi \), starts for both polarizations at a value in the second quadrant. As the angle of incidence increases, \( \phi \) tends towards 180° while \( \phi \) falls. The orange circle is centered on the origin and passes through the point \( y_0 \) and so it marks the boundary between the first and second quadrants. The radius of the orange circle is \( y_0 \). The product of the two admittances at the points of intersection of an isoreflectance circle with the real axis, is \( y_0^2 \). Geometry tells us, therefore, that the isoreflectance circle that passes
through the intersection of the orange circle and red line, is tangent to the red line, and corresponds to a minimum reflectance. Beyond that point, the reflectance for \( p \)-polarization rises. At grazing incidence the reflectances for both polarizations reaches 100%. The angle of incidence corresponding to the minimum \( p \)-reflectance, is called the \textit{Pseudo Brewster Angle} because of the resemblance to the curves for dielectric materials where the \( p \)-reflectance falls to zero.

The rule for calculating the retardance in reflection, \( \Delta \), from phase changes on reflection that are given in the normal thin-film convention, is

\[
\Delta = \varphi_p - \varphi_s \pm 180^\circ \tag{11}
\]

Thus the retardance starts at 180° at normal incidence, and falls with increasing angle. It has not quite reached 90° by the Pseudo Brewster Angle, but does reach it soon after. The corresponding angle is called the \textit{Principal Angle}. At grazing incidence, \( \Delta \) becomes 0°.

From Figure 7 we can calculate an approximate value for the Pseudo Brewster Angle. The square of the length of the line from the origin to the starting point is \( n^2 + k^2 \). The radius of the orange circle is \( y_0 \). The Pseudo Brewster Angle is, therefore, given by:

\[
\varphi_{PB} = \arccos \left( \frac{y_0}{\sqrt{n^2 + k^2}} \right) \tag{12}
\]

For silver in air at 550nm with \( n-ik = 0.055-3.32 \) the Pseudo Brewster Angle is calculated as 72.5° and that is close to the value indicated in Figure 8.

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Figure 8. The variation of reflectance of silver at 550nm as a function of angle of incidence in air.

Figure 9. The variation of the reflected retardance (or ellipsometric delta) as a function of angle of incidence for silver at 550nm.

Beyond Critical

In the normal way, when we are dealing with dielectric materials, Snell’s Law yields real propagation angles and we avoid the difficulty of equation 5. However, there are some rather special circumstances in which even with dielectric materials we find a similar problem. Let the incident medium and the emergent medium both be pure dielectrics, but let the incident medium be of greater refractive index than the emergent. This would be the situation, for example, when light is incident on the base of a prism from inside the prism. Snell’s Law gives for the angle of propagation in the emergent medium, \( \theta \), the expression:

\[
\sin \theta = \frac{n_0}{n} \sin \theta_0
\]

(13)

\( \sin \theta_0 \) can range from zero to unity while \((n_0/n)\) is greater than unity. Thus over a range of angles beyond a threshold value, the argument of the arcsin term in equation 13 is greater than unity, and \( \theta \), therefore, imaginary. The threshold value of \( \theta_0 \) is known as the Critical Angle, given by \( \arcsin(n/n_0) \). Fortunately the expressions we have derived for the general absorbing material, equation 7 and equation 8 can be applied to this case. We simply set \( k \) to zero so that the values beyond the critical angle become:

\[
\eta_p = -i \sqrt{n_0^2 \sin^2 \theta_0 - n^2} \cos \theta
\]

\[
\eta_s = \frac{n^2}{\eta_p}
\]

all in free space units.

The behavior of the admittance of the emergent medium is then as shown in Figure 10. From normal incidence, the \( s \)-admittance falls, reaching zero at the critical angle, while the \( p \)-admittance rises to infinity. Beyond the critical angle the \( s \)-admittance becomes negative imaginary and gradually moves down the negative limb of the imaginary axis to reach infinity at grazing incidence. The \( p \)-admittance, on the other hand, flips to the top of the positive limb of the imaginary axis, and then, with increasing angle of incidence, moves down the axis to reach the origin and a value of zero at grazing incidence. Since the admittances are imaginary, the reflectance of the surface is 100%, a phenomenon known as Total Internal Reflection, or TIR. The region we are interested in here is that beyond critical, and especially for \( p \)-polarization.

Figure 10. Diagram illustrating the behavior of the modified admittances for a material exhibiting the critical angle.

Surface Plasmon Resonance

The \( p \)-polarization admittance is positive imaginary beyond the critical angle. This is responsible for many exceptionally interesting phenomena. We shall consider just one example here, that of what is usually known as Surface Plasmon Resonance.

Let \( p \)-polarized light be incident on the base of a prism at an angle of incidence beyond the critical angle for the combination of incident medium and emergent medium materials. Now let the base of the prism be coated with a thin layer of high-performance metal such as silver. This will not alter the nature of the critical angle, which is determined by incident and emergent media. Let the angle of incidence be varied from the critical angle to grazing incidence. As the angle varies, the modified emergent medium admittance for \( p \)-polarized light travels down the positive limb of the imaginary axis, from infinity at the very top, to zero at the origin. The metal locus will be one of the family of circles with pivot point \(-\eta_p = (-n+ik)\cos \theta_0\) similar to Figure 2, but
with the pivot point gradually moving down the imaginary axis with increasing incidence. However, this rate of fall is quite small compared with the rate at which the admittance of the emergent medium falls down the axis.

Clearly, there will be a particular angle of incidence at which the metal locus will pass through, or would pass through if extended, the point \( y_0 \) on the real axis, that is the admittance of the incident medium. Under those conditions it is necessary only for the metal locus to be of the correct length for the film to present zero reflectance. This condition will exist when the emergent medium admittance is close to the pivot point of the metal. Since, for a metal such as silver, this pivot point is just on the other side of the imaginary axis, the movement of the emergent medium admittance will exert tremendous leverage, making the end point of the metal locus travel at enormously increased speed, so that it will whip very rapidly through \( y_0 \). The smaller \( n \) is for the metal, the closer is the pivot point to the axis, and the faster is the movement of the locus end point.

The result of this movement is a narrow dip in reflectance, confined to a very small range of angles. Outside that range the reflectance of the silver layer will be high. The dip in reflectance as a function of angle of incidence has all the features of a sharp resonance. Physically it is associated with a surface plasma wave that travels along the outer surface of the metal layer. It is known as a Surface Plasmon Resonance, sometimes abbreviated to SPR.

![Figure 11. The admittance loci of the silver layer 0.05° before resonance, on resonance, and 0.05° after resonance. The distance between the end points is huge compared with the distance between the starting points.](image)

Clearly the thickness of the metal film, \( d \), is the principal determinant of the depth of the resonance. The width of the resonance is largely a function of the distance of the pivot point from the imaginary axis, in other words the value of \( n \). The angular position of the resonance is

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![Graph showing the relationship between reflectance and incident angle](image)

Figure 12. A surface plasmon resonance in silver. The wavelength is 632.8nm. Incident medium glass n = 1.5151, silver n–ik = 0.00658–44.0452 and d = 54.435nm. Air, n = 1.000, is the emergent medium.

largely a function of k. There are thus three readily measurable attributes of the resonance that are connected principally with the three attributes, n, k and d, of the metal film, making the extraction of these parameters straightforward and reliable. In fact, this is one of the most sensitive techniques for the measurement of the optical properties of a high-performance metal. There are, of course, two solutions, because a minimum reflectance may be associated with a layer thicker than optimum, or thinner than optimum. The two solutions coincide when the minimum reflectance is zero. There are several ways of dealing with this problem. For example, the resonance can be biased so that the minimum reflectance is sufficiently far from zero that the two solutions are separated to the extent where one can be rejected. Alternatively, two wavelengths can be used, when the common thickness solution will be the correct one.

Suppose a thin layer of dielectric material is now added to the outer surface of the metal layer. Since the dielectric layer locus starts on the imaginary axis it will not leave it, but will simply move up the axis slightly, depending on its thickness. For the resonance to occur, therefore, the point corresponding to the emergent medium will require to be lower on the imaginary axis than before, implying a greater angle of incidence. Because of the sensitivity to angle, a quite thin layer will perturb the resonance perceptibly towards greater angles. This is the principle of a technique of incredible sensitivity for the detection of minute amounts of material. One tenth of a nanometre of material will open in December 2008 will be lower on the imaginary axis than before, implying a greater angle of incidence. Because of the sensitivity to angle, a quite thin layer will perturb the resonance perceptibly towards greater angles. This is the principle of a technique of incredible sensitivity for the detection of minute amounts of material. One tenth of a nanometre of material can be detected in this way. The technique is used in a wide range of applications and especially in the study of cellular membrane protein binding [5], of immense important in cellular biochemistry. Figure 13 shows a typical example.

Conclusion
The admittance diagram is a very powerful technique for appreciating the behavior of thin-film optical coatings. Although metals are much more complicated than dielectrics, nevertheless their properties are readily understandable in the admittance diagram. Very often approximate techniques are all that is required. For accurate calculations and accurate admittance loci we can always turn to the computer.

Figure 13. The resonance of Figure 12 (red) where the silver layer has been overcoated with 0.5nm of Ta$_2$O$_5$ (blue). The shift in the resonance is easily measurable.

References

Angus Macleod is currently President of the Society of Vacuum Coaters. He was born and educated in Scotland. Then in 1979 he moved to Tucson, where he is President of Thin Film Center, Inc. and Professor Emeritus of Optical Sciences at the University of Arizona. His best-known publication is Thin-Film Optical Filters, now in its third edition. In 2002 he received the Society’s Nathaniel H. Sugerman Memorial Award.

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