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IR SURFACE PLASMON SPECTROSCOPY

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Résumé - On passe en revue les avantages et les pièges de la spectroscopie de plasmons de surface dans l'infra-rouge.

Abstract - The practicality and pitfalls of IR surface plasmon spectroscopy are reviewed.

I - INTRODUCTION

Because infrared surface plasmons (SP's) propagate for many wavelengths on metal surfaces, a great deal of effort has gone to characterizing the properties of this unusual surface probe /1,2/. A direct analogy with plane wave spectroscopy does not exist. Developing efficient SP couplers for the infrared has been particularly challenging since neither the SP attenuation coefficient nor the wave height scales with frequency. Couplers not only excite the SP mode but also excite some of the plane wave modes which occur at the same frequency. Such "surface skimming" waves have been particularly hard to eliminate in the far infrared spectral region.

If these experimental problems can be overcome then a new kind of measurement will be possible. Because the SP attenuation coefficient is directly proportional to the metal reactivity, a measurement of this attenuation length together with an infrared reflectance measurement at the same frequency determine both parts of the complex dielectric function of the metal with equal precision. This combination of techniques may provide the first independent measurement of the infrared electron mass of metals.

Some progress has been made toward this goal. SP's have been generated both with single frequency lasers and also with broadband continuous sources /3,4/. Measurements have been made of the transmission of IR surface plasmons across a variety of metal surfaces. For the bare metal agreement is obtained with Drude model predictions while for dielectric coated metals some discrepancies remain. By making use of a novel interference phenomenon which is unique to inhomogenously propagating waves, it has been possible to measure the SP index of refraction for coated metals.

II - SURFACE PLASMONS ON BARE METAL SURFACES

A - Model Calculations

To emphasize the unusual features of SP propagation on a metal at a given infrared frequency, it is useful to compare the results with those obtained for plane waves reflected from a metal surface. The IR absorption by a metal at room temperature can be described by the classical skin effect since the mean free path, \(\varphi_T\) is much smaller than the skin depth \(\delta\). The Drude formula for the conductivity

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$\sigma = \left( \frac{\omega_p^2 \tau}{4\pi} \right) (1 - i\omega \tau)^{-1}$ \hspace{1cm} (1)

correctly describes the entire regime: when $\omega \tau << 1$ the conductivity is limited by $\nu_{FT}$ and when $\omega \tau >> 1$ the accelerating field reverses sign before a scattering process occurs. Because much of the work described below is for good conductors in the 10 $\mu$m wavelength region, the $\omega \tau >> 1$ limit will be emphasized.

The metal is taken to be in the (-)x half space with its boundary in the $(y,z)$ plane. The surface impedance for a normally incident plane wave polarized in the $z$ direction is

$\zeta = \frac{\hat{E}_z(0)}{\hat{H}_y(0)} = \varepsilon^{-1/2}$ \hspace{1cm} (2)

where $\varepsilon = i\frac{4\pi}{\omega} \sigma/\omega$. Let $q_0 = \omega/c$, the free space wavevector, then the wavevector in the metal is

$\hat{q} = -i\frac{q_0}{\zeta}$ \hspace{1cm} (3)

and the penetration depth of the field amplitude is

$\delta = [\text{Re} \hat{q}]^{-1}$. \hspace{1cm} (4)

For the IR $\omega << \omega_p$ and the absorptivity

$A = 1 - R = 4 \text{ Re } \zeta = 4\tau$. \hspace{1cm} (5)

In the relaxation region where $\omega \tau >> 1$

$\zeta = (2\omega_p \tau)^{-1} - i\frac{\omega}{\omega_p}$.

(6)

Since $x < 0$ the surface reactance is inductive. Equation (4) becomes

$\delta = \frac{c}{\omega_p}$ \hspace{1cm} (7)

and Eq. (5) simplifies to

$A = 2/\omega_p \tau$. \hspace{1cm} (8)

Now let's find similar relations for a SP bound to the air-metal interface. To take into account that this TM mode is localized at the surface and propagates in the $z$ direction, the $H$ field is assumed to have an inhomogenous wave form, namely

$\hat{H}_y(x,z) = \begin{cases} e^{-iq_0x} e^{i\frac{\omega}{\omega_p}z} & x > 0 \\ e^{-iq_0x} e^{i\frac{\omega}{\omega_p}z} & x < 0 \end{cases}$ \hspace{1cm} (9)

Combining this field with Maxwell's equations one finds that
The surface impedance for the surface plasmon mode is slightly larger than the impedance for plane waves. In order to compare the SP and the plane wave results, we describe the SP properties in terms of the plane wave surface impedance values. In the same limit as the plane wave problem the SP wavevectors simplify to

\[
\hat{q}_\parallel = q_0 \left( 1 - \frac{\theta^2}{2} \right).
\]

\[
\hat{q}_{\perp,a} = i q_0 \hat{\zeta}
\]

\[
\hat{q}_{\perp,m} = -i q_0 / \hat{\zeta}
\]

where \( \hat{\zeta} \) is determined from Eq. 6. In most of the infrared region the behavior of the SP fields is dominated by the real parts of the wavevectors. These quantities are plotted for Drude silver as a function of frequency in Fig. 1.

Note that in the infrared, \( q_\parallel \) very nearly follows the light line, \( q_{\perp,a} \) is roughly constant and \( q_{\perp,m} \) grows quadratically with frequency. From Eq. 14 the SP fields become increasingly confined to the neighborhood of the metal surface with increasing frequency.

\[
\gamma = \left[ \text{Re} \left( \hat{q}_{\perp,a} \right) \right]^{-1}
\]

depends only on the surface reactance while the depth which the field amplitude penetrates into the metal is the same as Eq. 4, namely

\[
\delta_{SP} = \left[ \text{Re} \left( \hat{q}_{\perp,m} \right) \right]^{-1} = \delta.
\]

The SP attenuation coefficient is
A comparison of Eq. 15 and Eq. 5 demonstrates that SP attenuation and IR absorptivity probe different properties of the metal. This difference also shows up in another way. By Equation 11, \( \hat{q}_y \neq q_0 \) and plane waves cannot directly couple to SP's. Prism, edge and grating couplers are used to overcome this wavevector difference between plane waves and the bound mode /5-9/.

B - Measured SP Attenuation Coefficients

A variety of SP attenuation coefficients have been reported for Drude-like metals in the IR /9-15/. In the far infrared investigators have reported anomalously large attenuation coefficients for a number of surfaces /16/. However two recent studies have concluded that the present evanescent wave coupling techniques are too inefficient for coupling SP's at 84 cm\(^{-1}\) and the SP mode is obscured by a transmitted bulk wave packet /17,18/. It is the spreading of this packet which accounts for the anomalously large attenuation coefficients which have been reported. The reason the evanescent field coupling technique can be used successfully in the IR region but not in the FIR is that the SP field profile height does not scale with wavelength whereas the evanescent field height which is the driving source does.

The evanescent field coupler has been used with somewhat more success in the 1000 cm\(^{-1}\) region but even there the measured attenuation coefficient of Au ranges over a factor three /10,11,14,15/. One possibility is that the integrity of the thin film surfaces vary widely. A measurement of the d.c. resistivity of films would provide some degree of normalization against this fabrication problem but not all investigators have reported resistivities. Another possibility is that one has run into the same fundamental problem which was observed in the far infrared, namely a mismatch between the SP profile height and the evanescent field profile height. The end result of a mismatch is that at any dielectric interface or edge discontinuity, colinear radiative and SP waves are generated. There is now some evidence that distinguishing between these two signal channels with the two prism coupler in the 10 \( \mu \) wavelength region may be a more subtle problem than previously recognized. Remeasurement of the SP attenuation coefficients of Ag and Au in the 10 \( \mu \) wavelength region with a different coupling geometry than earlier investigators have given much smaller values /19/. Good agreement between experiment and the Drude model is obtained when the IR relaxation time includes both the d.c. contribution and diffuse scattering of the electrons at the metal surface.

III - SP's ON DIELECTRIC COATED METALS

A - Model Calculations

The calculation of the SP attenuation coefficient and index of refraction is a straightforward extension of the bare metal case except now the results must be determined numerically /20/. For the thin film limit approximate analytic expressions can be obtained and we consider that case /21/.

The metal is separated from the air by a dielectric coating of thickness \( d \) and dielectric constant. In the infrared \( |\epsilon| \ll \eta \) and for thin films where \( d \ll d_c = \lambda/4(\eta-1)^{1/2} \), the complex wavevector can be written as

\[
\hat{q}_y = q_0 \left[ 1 - \frac{\zeta^2}{2} + [\zeta^3 - (1 - \eta^{-1}) \zeta](iy) \right. \\
\left. + \frac{1}{2} (1 - \eta^{-1})^2 - 2(\eta - 1) \zeta^2 + \frac{\eta^2 - 4}{2} y^2 \right] 
\]

where \( y = q_0 d \).
For a Drude metal the attenuation coefficient is

\[
\alpha(d) = \alpha(0) \left[ 1 + (1 - \eta^{-1})\left(\frac{d}{\delta}\right) + 4(\eta - 1)(q_0d)^2 \right. \\
\left. + \eta(1 - \eta^{-1})^2\left(\frac{d}{\delta}\right)(q_0d)^2 \right]
\]  \tag{19}

where \(\alpha(0)\) is given by Eq. (15) and \(\delta = c/\omega_0\), the London penetration depth, when \(\omega t >> 1\) and \(\delta = c/(2\omega_0\sqrt{T})^{1/2}\), the classical skin depth, when \(\omega t << 1\). Equation (19) consists of four terms. The first term is the bare metal SP attenuation coefficient while the next three terms represent the increase in SP loss in the metal as induced by the coating. In Ref. (17) it is shown that if lattice absorption occurs in the dielectric coating so that \(\text{Im} \eta \neq 0\) then four additional terms appear in the attenuation coefficient. The ratio of the largest of these new terms to the largest term in Eq. (19) for the nonabsorbing coating is

\[
\frac{\text{Absorbing film}}{\text{Nonabsorbing film}} = \frac{2\omega t \text{Im} \eta}{\eta^2} \left(\frac{d}{\delta}\right).
\]  \tag{20}

If the thickness of the absorbing dielectric film is less than or comparable to the metal skin depth, then the nonabsorbing film limit given by Eq. (19) applies to both cases.

Experiments will be described below which measure the index of refraction of the SP in the relaxation region. From Eq. (18) we find

\[
\eta^2 - 1 = \text{Re} \left(\frac{q_\|}{q_0}\right) - 1 = (1 - \eta^{-1})(q_0^2d\delta) + \frac{1}{2} (1 - \eta^{-1})^2(q_0d)^2.
\]  \tag{21}

For SP's in the 1000 cm\(^{-1}\) region and film thickness \(d = 500\) A the two terms are comparable in size. For thicker films Eq. (21) is independent of the properties of the metal itself.

B - Infrared Measurements

1 - Attenuation

The experimental \cite{18} far infrared attenuation coefficients \(\alpha(d)\) as a function of Ge overlayer thickness, \(d\), are shown for Au and Pb in Fig. 2. Figure 2a shows the results of measurements on three different Au films. The error bars indicate the uncertainty in the determination of \(\alpha(d)\) from the transmission measurements made on a particular film. The somewhat larger scatter in the data may be due to effects associated with roughness which may differ from film to film.

The theoretical SP attenuation coefficient is given by Equation 15 and in the Drude limit \(\alpha(0)\) is proportional to the d.c. resistivity, \(\rho\), so that

\[
\alpha(0) = \frac{\omega^2}{4\pi\rho}.
\]  \tag{22}

Equations 19 and 22 have been used to calculate the value of the surface wave attenuation coefficient for both the Au and Pb films. The solid curves in Fig. 2a and b correspond to the measured film d.c. resistivities \(\rho(Au) = 8\ \mu\Omega\ cm\), curve 2, and \(\rho(Pb) = 32\ \mu\Omega\ cm\). The discrepancy between these (Drude) theory lines and experiment for large \(d\) is of undetermined origin (it may be due to \(d\) dependent roughness). However, for the purposes of this review we will focus solely on the much larger discrepancy in the small \(d\) region. These investigators point out that the negative slope of the experimental \(\alpha(d)\) (in Fig. 2a and 2b for \(d < 0.5\ \mu\)) makes it unlikely that the SP attenuation coefficient is actually being measured in
this regime of overlayer thickness. It is concluded /18/ that the SP mode is obscured by a transmitted bulk wave packet in the thin film region. It is the spreading of this packet which accounts for the anomalously large attenuation coefficients reported earlier /16/.

In Fig. 3 some measured values of the SP attenuation coefficients as a function of film thickness are shown for CuO on Cu /12/ and Ge on Ag /21/ in the 10 μm wavelength region. Both of these dielectrics are thought to be nonabsorbing in this wavelength region but neither set of data agrees with theory. The dependence of the SP attenuation coefficients for Ge coated Ag films have been analyzed in some detail /21/ and we review these results here.
The values of $\alpha(0)$ measured for the Ag films agree with those expected from the measured d.c. resistivities. Given $\alpha(0)$ and $\omega_p$, the nearly straight line in Figure 3 labeled theory results from Eq. (19). The calculated slope is substantially less than that measured. The investigators were not able to improve the agreement between theory and experiment by introducing absorption in the Ge.

Another surprising aspect of the thickness dependence data is that the straight dashed line through the data extrapolates back to the bare metal SP value. If the mean free path of the electrons within a skin depth of the surface was reduced by the presence of the Ge in or on the metal, if the surface roughness was enhanced by the coating or if the interface states in the Ge were important, the straight line should extrapolate back to a value somewhat larger than the bare SP value. This conclusion follows since the slope and the intercept of Equation 19 are not independent parameters as long as $\omega_p$ is fixed.

2 - Index of Refraction

The SP index of refraction has been measured by making use of a novel interference phenomenon which is unique to inhomogeneous propagating waves /20/. The propagation of radiation across a step discontinuity in the overlayer thickness can be viewed in terms of the coupling of the normal modes on one side to the normal modes on the other. In particular, consider a SP on the bare metal, traveling toward the step discontinuity produced by a thin dielectric coating. Since the discontinuity is small, reflection and refraction are small. One might expect the incident SP to couple predominantly to the SP of the coated region since both are bound modes; however, Maxwell's equations require that the tangential E and H fields be continuous across the step at all heights above the surface. Even for fairly thin overlayers $d \sim 0.02\, d_c$, the range of the SP above the coated metal surface is much less than that of the SP above the bare metal /21/. The boundary conditions at the coating edge can be satisfied only if the incident SP produces unbound bulk radiation in addition to the transmitted SP. For thicker overlayers $d > d_c/2$ the coated-metal SP is so compressed that the incident bare-metal SP cannot couple to it and almost all of the incident intensity is converted to bulk radiation. For thicknesses such that $0.02 < d/d_c < 1/2$ the incident SP launches both bulk and SP radiation. This bulk radiation is produced in the form of a packet traveling in the forward direction and spreading slowly in width. The SP travels along the coated surface with a phase velocity $c/n_1$, while the phase velocity of the bulk wave packet which travels above the overlayer is $c$. At the far edge of the overlayer, of length $\lambda$, the SP and bulk wave packet both contribute to the transmission of a bare-metal SP. However, these two contributions will in general no longer be in phase. The total intensity of the resultant SP launched at the trailing edge of the coating can be written

$$I(\lambda) = I_{SP}(\lambda) + I_B(\lambda) + 2[I_{SP}(\lambda)I_B(\lambda)]^{1/2} \cos[(n_1-1)q_0\lambda],$$

where $I_{SP}(\lambda)$ and $I_B(\lambda)$ are the component intensities. A bulk wave packet is also launched at the trailing edge with an interference term complementary to that of the SP. The first two terms in Equation 23 decrease monotonically with increasing overlayer length $\lambda$:

$$I_{SP}(\lambda) = e^{-\alpha \lambda}, \quad I_B(\lambda) = 1/\lambda.$$

From the third term in Equation 23, the spatial period of the interference is

$$\Delta \lambda = \frac{\lambda}{n_1 - 1}.$$
The difference in index of refraction of the SP wave and the bulk wave can be estimated from Equation 21. Because \( n_t - 1 \) is small, large interference periods will be produced by relatively short wavelength radiation.

To test these conclusions the investigators evaporated Ag and Au films on KCl couplers. Over part of these rectangularly shaped films thin Ge overlayers of a triangular shape were then deposited.

The SP was launched from a CO\(_2\) laser beam at one edge of the metal film by means of the edge coupling technique. At the corresponding point on the opposite edge of the metal the SP produced at the trailing edge of the coating coupled into the dielectric substrate and was detected. The length \( \lambda \) of the overlayer region probed by the beam was continuously varied by translating the film assembly in the plane of the surface but perpendicular to the beam direction. The transmission was measured as a function of \( \lambda \) for fixed overlayer thickness \( d \) and CO\(_2\) laser frequency \( \omega \).

An example of the observed transmission vs \( \lambda \) showing interference between a SP and bulk radiation is presented in Fig. 4(a) along with the Fourier transform of the interferogram in Fig. 4(b). Values of the interference period \( \Delta \lambda \) are obtained either from the separation of the local maxima of the interferogram [Fig. 4(a)] or from the position of the peak in its Fourier transform [Fig. 4(b)].

![Graph showing transmission vs overlayer length](image)

**Fig. 4 - SP index of refraction measurement of a dielectric coated metal.** (a) SP transmission across a Ge-coated Ag film vs optical path. The Ge coating is \( d = 0.2 \) \( \mu \)m thick \( (d/d_c = 0.3) \) and the laser frequency is 975 cm\(^{-1}\). (b) Fourier transform of the interferogram in (a). Measurements like these have been used to study the spatial period of interference vs laser frequency. Because of the relatively large value of \( d/d_c \) the approximate expression given by Eq. 21 produces a 20% error. Increased precision was obtained by numerical calculation. Good agreement was found between theory and experiment. After Ref. 17. It should be noted that for these relatively thick dielectric coatings, the SP index is independent of the properties of the metal itself.

**IV - CONCLUSIONS**

Of fundamental importance is the way the parameters which describe the electrodynamics of the metal enter the SP mode. It is different than for plane wave spectroscopy. The appearance of the product of the surface resistance and surface reactance in Eq. 15 is an important result and requires some explanation. In the IR most of the field intensity of the SP mode is in the air above the metal. The amplitude of the magnetic field at the surface is inversely related to the height
of the mode above the surface. Since the attenuation coefficient depends on the amplitude of the field at the surface then by Eq. 14 it must be proportional to the surface reactance. A measurement of both \( \alpha \) and \( A \) for the same metal surface would enable one to separately determine \( \omega_p \) and \( \tau \). Although it has been known for many years that the IR dependencies of these two parameters should provide a great deal of information about the dynamics of the electron-phonon interaction \(^{123}\) such a determination with plane wave measurements has proven to be elusive.

The same reason which makes the SP attenuation measurement attractive as a fundamental probe makes it difficult to use experimentally. To obtain efficient SP generation the evanescent field distribution generated at a coupler by the spectrum of plane waves must match the spatial distribution of the fields associated with the bound mode. Antennae for plane waves scale as \( a^{-'} \) but the height of the SP varies as \( \omega^{-2} \). The conclusion is that a coupler designed to work efficiently in one frequency region cannot be simply scaled to give the same performance in another frequency range. If it is matched to produce SP's in one frequency region then it is likely that in the second, a wave packet of surface skimming plane waves could be the dominant signal. The experimental identification of these two components is not simple. The plane wave packet diffracts as it moves across the surface so an "apparent" attenuation coefficient can be measured for this component as well.

From this discussion it is clear that the key parameter for understanding the infrared properties of SP's is the height to which the SP fields extend above the substrate. The interference between SP's and plane waves observed with the SP interferometer is one demonstration of the importance of this parameter. The substantial coupling of the bound SP to the unbound radiation, which can occur whenever the nature of the interface supporting the SP changes abruptly, is proving to be one of the more subtle features of SP spectroscopy.

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