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THE USE OF SURFACE ELECTROMAGNETIC WAVES TO MEASURE MATERIALS PROPERTIES

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An elementary introduction to surface electromagnetic waves (SEW) is presented. The emphasis is on those features of SEW which make them useful for measuring optical properties of thin layers on metals. The so-called two-prism technique for making such measurements is discussed, some preliminary experimental results are given, and some possible applications are presented.

1. Introduction

Surface electromagnetic waves (SEW) or surface polaritons have recently received considerable attention, resulting in a sudden increase in the number of review articles [1–7]. No attempt is made to present a comprehensive review here, but rather to consider only the use of SEW to measure materials properties, particularly of thin layers on metal substrates. Ferroelectrics are also considered briefly. Attention is confined to optical studies, omitting the large amount of work using other methods.

First, SEW is considered at a metal-vacuum interface, and then at a three-layer system of a metal with a coating. Some preliminary experimental results are given. Mathematical details are omitted, the emphasis being on illustrating those properties of SEW which make them useful for materials studies and more particularly for surface studies.

2. Two media

To begin, a metal-vacuum interface is shown in fig. 1. Surface electromagnetic waves on a metal are usually called surface plasmons. The interface lies in the xy-plane and the SEW are considered to propagate in the x-direction. The metal has a complex dielectric constant $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The solutions to Maxwell's equations required are surface waves in the sense that both the electric and magnetic fields associated with the SEW decay exponentially as one moves away from the interface in both the plus and minus z-direction. Using Maxwell's equations and the

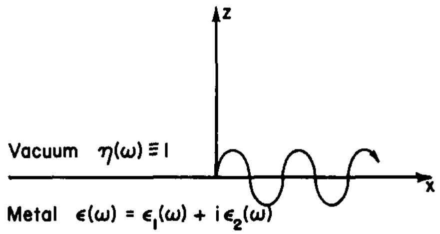

Fig. 1. Metal-vacuum interface showing coordinate system used.

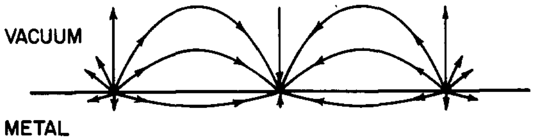

Fig. 2. Electric field pattern for a surface electromagnetic wave on a metal. Accompanying magnetic vields are perpendicular to the page.

usual boundary conditions, it is found that the only surface wave solutions are the analogs of plane waves with electric field components in the x- and z-directions and only one magnetic field component which is in the y-direction. Hence, these solutions are called transverse magnetic modes. Explicitly, the electric fields are given by [8]

$$\boldsymbol{E}_{\mathrm{b}} = E_0(1, 0, \mathrm{i}\, k_x/k_{\mathrm{b}z}) \exp(\mathrm{i}\, k_x x) \exp(-k_{\mathrm{b}z} z) \tag{1}$$

in the vacuum, and by

$$\boldsymbol{E}_{\mathrm{a}} = E_0(1, 0, -\mathrm{i}\, k_x/k_{\mathrm{a}z}) \exp(\mathrm{i}\, k_x x) \exp(k_{\mathrm{a}z} z) \tag{2}$$

in the metal. Note that the factor i was not written before k_z because exponential decay is expected in the z-direction. Hence, the real part of the z-component of the propagation vector $\boldsymbol{k}$ gives the exponential decay. The electric field vector is sketched in fig. 2. Note that this electric field pattern is just what would be expected from a sinusoidal surface charge distribution traveling along the interface. The fact that the net charge on the surface is zero forces the electric fields to fall to zero as we move away from the interface.

An important feature of the SEW is that its wavelength is shorter than the wavelength of a photon of the same frequency in vacuum. It is this property which prevents the surface wave from propagating away from the surface as a free photon or ordinary electromagnetic wave. It is customary to consider, not the wavelength λ but rather the propagation vector $k = 2\pi/\lambda$. It is then found that the frequency dependence of the x-component of the wave vector is [8,9]

$$k_x(\omega) = \frac{\omega}{c}\left(\frac{\epsilon(\omega)}{\epsilon(\omega) + 1}\right)^{1/2} = k_{1x} + \mathrm{i}\, k_{2x}. \tag{3}$$

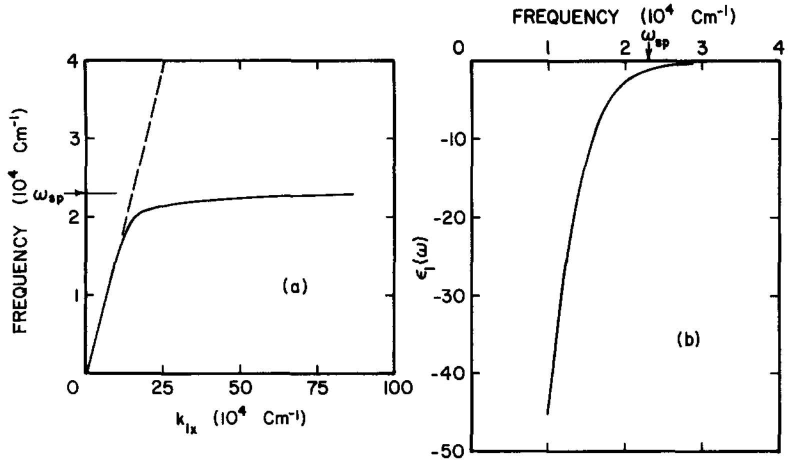

Fig. 3a. Dispersion curve for surface plasmons on Au. 3b. Sketch of $\epsilon_1(\omega)$ versus ω for copper. Optical data from ref. [6] of ref. [23] of this paper.

This relation is called the dispersion curve. A typical plot of ω versus $k_{1x}(\omega)$ is shown in fig. 3. Recall that for an ordinary electromagnetic wave in vacuum, the dispersion curve is simply

$$k = \omega/c, \tag{4}$$

which is the straight line in fig. 3. This line is called the light line. In the middle and far IR, $\epsilon(\omega)$ is large and negative for metals. Hence, eq. (3) tells us that $k_x \gtrsim \omega/c$, and the dispersion curve for the surface plasmon will lie near the light line as seen in fig. 3. As $\epsilon(\omega)$ approaches -1, the denominator under the square root in eq. (3) becomes small and the dispersion curve bends away from the light line.

It is shown that in order to have surface wave solutions with exponential decay into the vacuum an additional requirement must be met [8], namely

$$\epsilon_1(\omega) < -1. \tag{5}$$

The frequency labeled ω_{sp}, where k_{1x} becomes infinite in fig. 3, is that frequency for which $\epsilon(\omega) = -1$. Note that dispersion curves are usually plotted as if absorption were neglected, i.e. ϵ_2 is set identically zero. Then $\epsilon_1(\omega)$ for a metal looks approximately as shown in fig. 3b. However, eq. (5) is valid for complex $\epsilon(\omega)$ and the imaginary part of k_x ($\equiv k_{2x}$) tells how fast an SEW decays due to absorption. The surface plasma frequency ω_{sp} lies in the visible or UV for many metals. On metals, therefore, surface waves exist from very long wavelengths to visible wavelengths. Ionic crystals have dielectric functions satisfying eq. (5) between their transverse and longitudinal optic phonon modes. SEW on such crystals are often surface phonons, and the frequency range is in the far IR.

The real part of k_z characterizes the depth to which the electric and magnetic

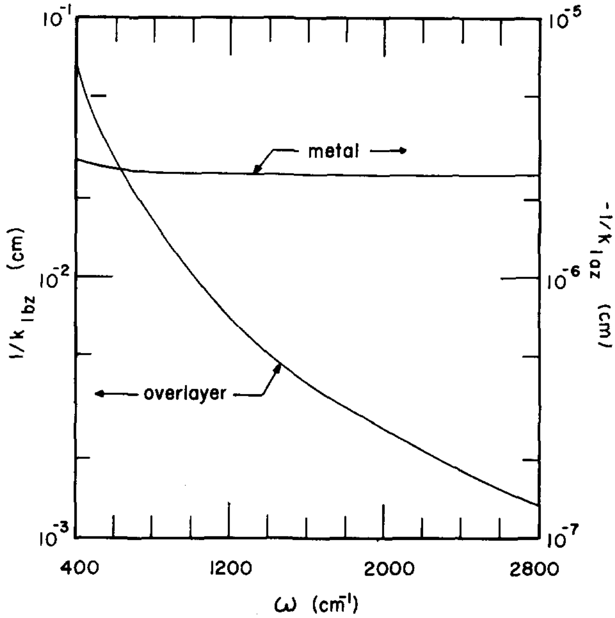

Fig. 4. Decay distance, $1/k_{1az}$, of electric and magnetic fields into copper (right ordinate) and extension distance into vacuum (left ordinate). Bulk optical constants for copper as in fig. 3.

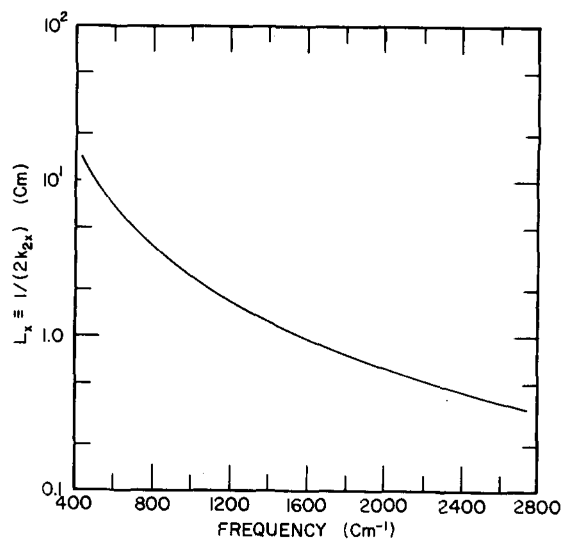

Fig. 5. Propagation distance $L_x \equiv 1/2k_{2x}$ as a function of frequency for copper. Bulk optical constants for copper as in fig. 3.

fields penetrate into the metal and the air. Fig. 4 shows the 1/e penetration depth for Cu and vacuum as a function of frequency. Note that the penetration into the metal is just the classical skin depth (≈300 Å), while the penetration into the vacuum is considerably larger. It is obvious then, that SEW sample more than what is considered the surface, in the sense of a monolayer. However, the absorption of surface waves is sensitive to monolayers.

How far do SEW propagate on metals? After all, a metal is highly absorbing and an ordinary bulk electromagnetic wave propagates only a skin depth (≈200–300 Å). But for a SEW, most of the energy associated with the wave is above the metal surface, and so the propagation distance is much longer. The propagation distance, $L = 1/(2k_{2x})$, can be obtained from eq. (5). L_x for Cu is shown as a function of frequency in fig. 5. Note that macroscopic propagation lengths ($L > 1$ mm) exist for frequencies less than 2 μm.

3. Three media

We now turn to systems which are more to our purpose. One such system consists of a metal which can propagate SEW, an overlayer which does not support SEW and finally air or vacuum above the overlayer. The overlayer has a complex dielectric function $\eta(\omega) = \eta_1(\omega) + i\eta_2(\omega)$, see fig. 6. This problem has been studied by electrical engineers under the name of a grounded dielectric plane [10,11].

It is assumed that the overlayer thickness d is very large. It can then be shown that in the middle and far IR ($\lambda \gtrsim 1$ μm) that [12]

$$L_x = 1/\alpha, \tag{6}$$

where α is the absorption coefficient of the overlayer material. Thus, this method can be used to study the optical properties of materials which do not themselves support SEW. A more complicated expression, including losses in the metal substrate may be found in ref. [12]. Note that a layer a few wavelengths thick is semi-infinite in effect since k_{1z} in the overlayer is increased considerably from its value in vacuum.

Turning now to thin layers, transverse electrical (TE) modes become possible, but we consider only transverse magnetic (TM) modes. These modes are wave-guide type modes (oscillating fields) in the slab with exponential decaying fields in the metal and vacuum. The dispersion curve can become quite complex, particularly if the layer b has

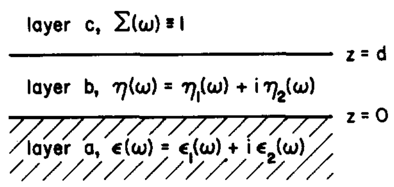

Fig. 6. Three-media system of metal, overlayer of thickness d, and vacuum.

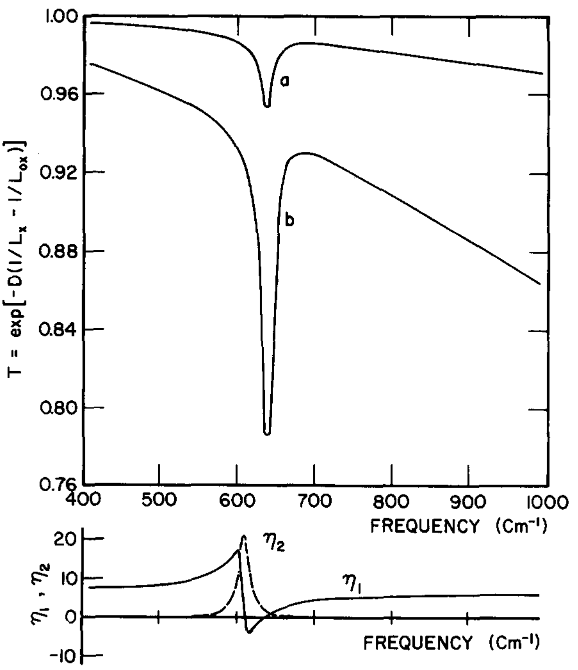

Fig. 7. Normalized transmission $T(\omega, D)$ for Cu–Cu_2O–vacuum with D = 10 cm. Curve a: monolayer of Cu_2O (d = 2.3 Å). Curve b: five monolayers of Cu_2O (d = 11.5 Å). The dielectric constants for Cu_2O from ref. [23] are at the bottom of the figure (from ref. [13]). Data for copper as in fig. 3.

regions of large absorption where η_1 becomes negative [13,14]. Rather than present complete details (see refs. [13] and [14]), a rather simple system consisting of a copper substrate (layer a) covered with a thin Cu_2O film (layer b) will be considered. Layer c is air. It can then be shown that [14]

$$T(\omega, D) \equiv I(\omega, D)/I_0(\omega, D) = \exp(-2\pi\omega\Delta_2 D), \tag{7}$$

where $I_0(\omega, D)$ is the intensity measured with no oxide and $I(\omega, D)$ is the intensity measured with an oxide layer of thickness d. The parameter Δ_2 is related to the dielectric functions of the metal and oxide by [14]

$$\Delta_2 \approx \frac{4\pi\omega d}{(-\epsilon_1)^{1/2}} \frac{(\eta_1^2 + \eta_2^2 - \eta_1)\epsilon_2/2(-\epsilon_1) + \eta_2}{(\eta_1 + \eta_2\epsilon_2/2\epsilon_1)^2 + (\eta_2 + \eta_1\epsilon_2/2\epsilon_1)^2}. \tag{8}$$

Further approximations may be found in ref. [14] for various special cases. It is emphasized that these approximations, eqs. (8) and (9), are for thin films $[d \lesssim \lambda/(\eta_1)^{1/2}]$. Fig. 7 shows a plot of T versus ω for a Cu–Cu_2O system with a five

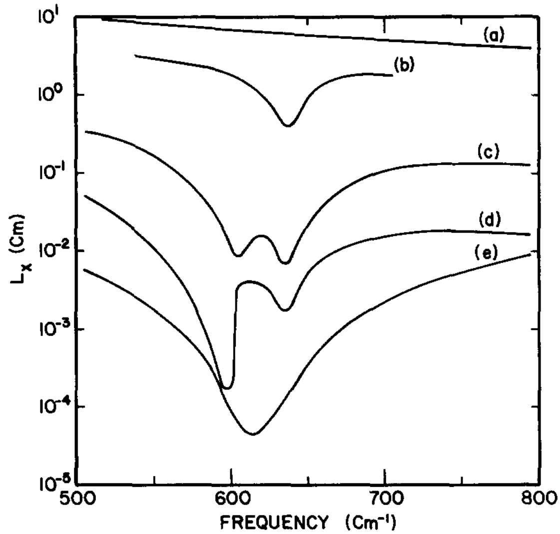

Fig. 8. Propagation distance L_x for Cu–Cu_2O–air for indicated thicknesses d of Cu_2O; (a) d = 0 A, (b) d = 500 A, (c) d = 5000 A, (d) d = 10000 A, (e) $d = \infty$. Note semi-log plot.

monolayer (d = 11.5 Å) oxide film in the region of the Cu_2O lattice resonance. The minimum value of T occurs at about ω_{LO}, the longitudinal optic phonon frequency (For an ordinary optical transmission measurement, T is a minimum at ω_{TO} where η_2 is a maximum.) As the layer becomes thicker, one can no longer use the approximation given in eq. (8), and the exact dispersion relation given in ref. [14] must be used. The results are shown in fig. 8, where as the oxide thickness increases the minimum in L_x moves from ω_{LO} to ω_{TO}, the transverse optic phonon frequency [15]. For the thin films, the peak absorption near ω_{LO} is apparently caused by an effect similar to that observed by Berreman [16] in his studies of the reflectivity of thin films. For very thin films ($d \lesssim \lambda$), the longitudinal optic modes become optically active due to the film boundaries. As the film becomes thicker and the boundaries are further apart, this effect becomes smaller and the absorption at ω_{TO} (where η_2 has its maximum) becomes most important.

4. Two-prism method

A number of experimental techniques have been used to study SEW. This discussion is confined to optical techniques and in particular to what has become known as the two-prism technique. The latter is the SEW analog of an ordinary optical transmission experiment.

Recall that a SEW has a wavelength shorter than an ordinary electromagnetic wave, and hence it cannot be excited by an ordinary incident electromagnetic wave.

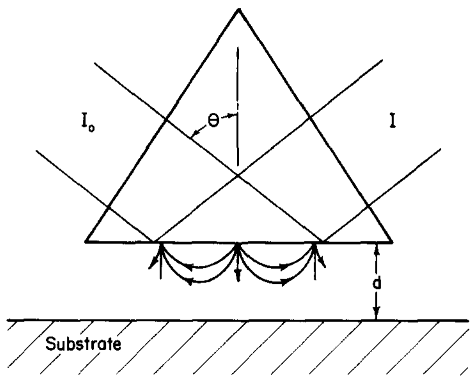

Fig. 9. Sketch of the evanescent field below a prism base where total internal reflection occurs. θ is greater than the critical angle for total internal reflection. Gap between prism and substrate has been exaggerated (after ref. [17]).

Otto [8] discovered a clever way to overcome this problem. In a material with an index of refraction n, the wavelength of an ordinary electromagnetic wave is λ/n. If total internal reflection takes place at the surface of this material, then an exponentially decaying field exists outside the surface and k_{1x} for this field is given by

$$k_{1x} = (\omega/c)\, n \sin\theta, \tag{9}$$

where θ is the angle of incidence inside the material. Fig. 9 shows a prism of index of refraction n, and the fields produced by a wave incident on the prism base at an angle greater than the critical angle for total internal reflection θ_c. This latter angle is given by

$$\sin\theta_c = 1/n. \tag{10}$$

It is seen that these fields resemble those outside a metal on which a SEW is propagating (fig. 2). Thus, by adjusting θ until the real part of the x-component of the propagation vector given by eq. (9) for the incident wave matches that given by eq. (3) for the SEW, excitation of the SEW by the incident field can occur. Thus, θ must be adjusted to satisfy

$$n \sin\theta = \mathrm{Re}\left(\frac{\epsilon(\omega)}{\epsilon(\omega)+1}\right)^{1/2} = k_{1x}. \tag{11}$$

The x-component of the momentum carried by the SEW is $\hbar k_{1x}$, so Otto's technique of frustrated total internal reflection allows momentum conservation by adjusting the momentum of the incident wave to match of the SEW.

This matching condition works two ways. It allows the incident wave to excite the SEW, but it also allows the SEW to couple out through the prism. Hence, the gap d must be adjusted to give a reasonable compromise between these two effects.

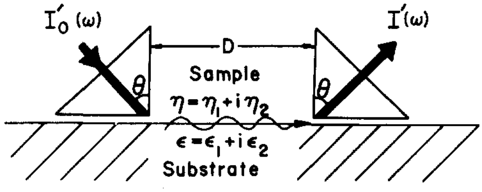

Fig. 10. Experimental arrangement for measuring the propagation distance of the SEW on the substrate (usually a metal) with the two-prism technique. $\epsilon(\omega)$ and $\eta(\omega)$ are the dielectric constants of the substrate and overlayer, respectively.

Then, if one measures the intensity of the light reflected from the prism base as a function of θ, a dip will be observed for the angle satisfying eq. (11).

To measure the optical properties of thin layers using SEW, a modification of the above single-prism technique is better. First suggested by Schoenwald et al. [18], it uses one prism to excite SEW and a second prism to receive them. This arrangement is sketched in fig. 10.

It was mentioned above that monolayers should be observable using this two-prism technique, at least monolayers with a reasonably strong absorption [13]. However, there are some experimental difficulties. The coupling angle for launching the surface wave (given by eq. (11)) is very well defined, requiring that the incident beam have a very narrow angular spread. In practice, this requires a laser source. Second, a reasonable L_x is required so that practical prism separations are possible. Fig. 5 shows that for a typical metal, this requirement restricts us to wavelengths longer than about 2 μm. This, however, still covers the range for molecular vibrational frequencies. It is just this region which is used by chemists for spectral indenti-

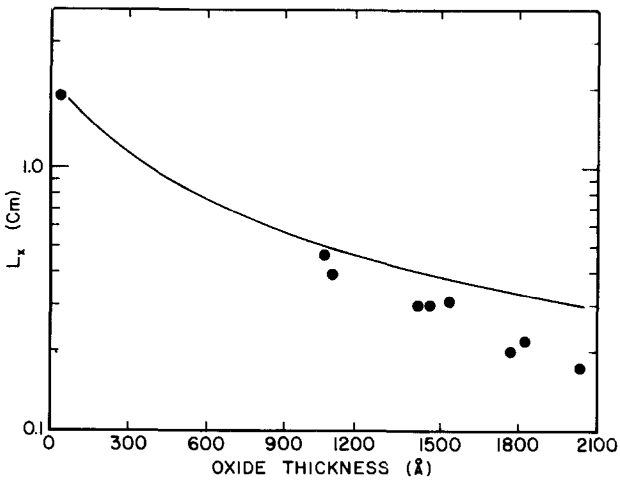

Fig. 11. L_x versus Cu_2O thickness on a copper substrate measured using a CO_2 laser operating at a wavelength of 9.62 μm.

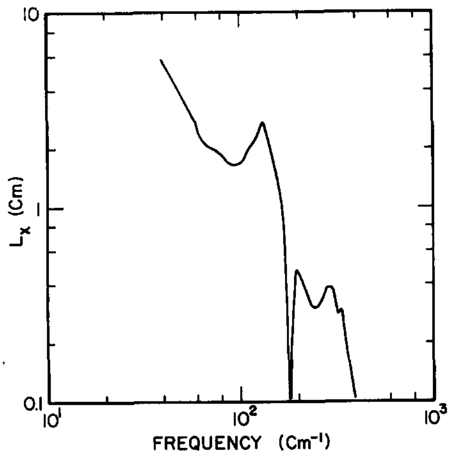

Fig. 12. Propagation distance of surface phonons on $SrTiO_3$. Optical data from ref. [24].

fication of compounds. It turns out that the gap d between the substrate and prism is of the order of a few to several tens of micrometers and hence does not provide great experimental difficulties. Mylar spacers can be used between the prism and substrate, for example.

Admittedly, relatively little data exists from the two-prism technique, and most of the existing data was taken to measure the optical constants of the metal substrate without an overlayer [18–21]. In our laboratory, SEW have been recently measured on a copper substrate with a Cu_2O overlayer produced by thermal oxidation [21]. A tunable CO_2 laser was used as a source. Fig. 11 shows the measured L_x versus oxide thickness for a wavelength of 9.62 μm. The solid curve was calculated using the theory discussed in section 3 and optical constants from the literature. This shows good agreement between experiment and theory for a simple system. More complicated systems consisting of a metal substrate with more than one overlayer have been considered theoretically [14], but no data on such systems have been reported.

We have been concerned mainly with metals as the SEW active substrate, but ionic crystals also meet the condition $\epsilon_1(\omega) < -1$ in the frequency region between ω_{TO} and ω_{LO}. Calculations also indicate that ferroelectrics in particular offer attractive possibilities in the far IR [22]. This is due to the large polarizabilities of these crystals at long wavelengths. As an example, fig. 12 shows L_x as a function of frequency for $SrTiO_3$, which, although not a true ferroelectric, has a large low-frequency polarizability.

5. Possible applications

SEW spectroscopy has been used to study the optical constants of metals, particularly thin films which may differ from the bulk material. Overlayers have been studied by using numerous variations of the single-prism excitation technique. Absorption studies of overlayers are just beginning, the Cu–Cu_2O oxide system mentioned above being among the first. This technique is also being applied to the study of physi- and chemisorbtion on metal surfaces. Other applications may be the study of surfaces prior to and after adhesive bonding, or the application of various coatings such as paints and glasses to metal substrates.

Acknowledgement

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