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LETTER TO THE EDITOR

Surface plasmon resonance halfwidths as measured using attenuated total reflection, forward scattering and photoacoustics

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Abstract. The resonance curves for surface plasmons on thin silver films were obtained for three spectroscopies: attenuated total reflection (ATR), forward scattering (FS), and combined photoacoustic–attenuated total reflection (PA–ATR). The positions of the resonance peaks and the halfwidths of the curves are compared and discussed. It is found that the peaks in FS spectroscopy are shifted towards smaller angles, and the peaks in PA–ATR spectroscopy are shifted towards larger angles of incidence compared with those obtained in ATR spectroscopy. The halfwidths for the PA–ATR are larger than those for the FS which in turn are larger than those for the ATR. The physical origin of the difference in resonance peaks and halfwidths is discussed.

Surface plasmons on metal films have been employed to investigate metal surfaces for many years. The resulting Lorentzian resonance curve in the angular spectra of surface plasmon wavevectors has been used to determine the real and imaginary components of the complex dielectic function of the metal film $\tilde{\varepsilon}(\omega)$ where ω is the frequency. Generally, the position of the resonance angle, a minimum in the case of attenuated total reflection (ATR), or a maximum in the case of forward scattering (FS), leads to an estimate of the real part ε', and the angular halfwidth leads to an estimate of the imaginary part ε''. To our knowledge there has been but a single study (Barnes and Sambles 1985) aimed at differentiating between the peaks of the resonance curves in the two spectra, or the resulting values of the components of the dielectric function.

In this work we have employed the above mentioned techniques, and furthermore we have employed the combined photoacoustic (PA)–ATR method (Inagaki *et al* 1981, 1982a, b, Talaat and Dardy 1983, Talaat *et al* 1985) to investigate the relation between the values obtained in the three methods. In the Kretschmann configuration of the ATR method (Kretschmann and Raether 1968), the measured reflected intensity in the case of visible EM waves and for silver films where $|\varepsilon'| \gg 1$, $|\varepsilon'| \gg \varepsilon''$ can be written as (Raether 1977)

$$R = 1 - 4\Gamma_i\Gamma_r/[(K_{\|} - K^m)^2 + (\Gamma_i + \Gamma_r)^2] \tag{1}$$

where $K^m = (K' + iK'')$ is the complex wavevector of the surface plasmon at the metal

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Table 1.

Spectra	Wavelength, λ (Å)	θ_{ATR} (deg) ±0.03	$\Delta\theta_{ATR}$ (rad) ±0.005	ε' ±0.425	ε'' ±0.066
ATR	5145	44.07	2.0×10^{-3}	−9.606	0.340
	4965	44.42	2.2×10^{-3}	−8.580	0.291
FS	5145	44.03	5.8×10^{-3}	−9.720	1.017
	4965	44.37	7.4×10^{-3}	−8.710	1.020
PA–ATR	5145	44.21	7.4×10^{-3}	−9.210	1.150
	4965	44.49	9.6×10^{-3}	−8.420	1.220

surface, $K_{\|}$ is the parallel component of the incident wavevector in the prism, and Γ_i, Γ_r are intrinsic dampings and radiation dampings of surface plasmons respectively. Also

$$K' = (\omega/c)n_p \sin\theta_{ATR} = (\omega/c)[\varepsilon_r/(\varepsilon_r + 1)]^{1/2} \tag{2}$$

and

$$K'' = (\omega/c)n_p \cos\theta_{ATR}\,\Delta\theta_{ATR} = (\omega/c)(\varepsilon_i/\varepsilon_r^2)[\varepsilon_r/(\varepsilon_r + 1)]^{3/2}. \tag{3}$$

Using the regular ATR experimental arrangement in the Kretschmann configuration (reflection) we obtain the angular spectra for this method, shown in figure 1. The radiation from an argon laser was TM polarised and incident at wavelengths of 5145 and 4965 Å on an Ag film of thickness 400 ± 8 Å. The values of the angles of resonance peaks θ_{ATR}, the half width, $\Delta\theta_{ATR}$ and the values of ε', ε'' obtained from these curves using the above expressions in equations (2) and (3) are shown in table 1.

In the case of FS angular spectra in the Kretschmann configuration, the differential scattered intensity is given by (Raether 1983)

$$dI/(I_0\,d\Omega) = \tfrac{1}{4}(\omega/c)^4(\sqrt{\varepsilon_0}/\cos\theta_0)\,|t^p(\theta_0)|^2\,|w(\theta)|^2\,|s(\Delta K)|^2 \tag{4}$$

where $\sqrt{\varepsilon_0}$ is the refractive index of the prism, θ_0 is the angle of the incoming light I_0, $t^p(\theta_0)$ is the Fresnel transmission coefficient and its square $|t^p(\theta_0)|^2$ is related directly to the Lorentzian in the expression for R in equation (1), $w(\theta)$ is the dipole radiation function and $s(\Delta K)$ describes the roughness spectrum.

In our arrangement, the scattering angle was fixed at $\theta = 0°$ and the detector was placed along the perpendicular to the Ag/air interface and close to the metal surface. The scattering intensity shows a peak as a function of θ where t^p has a maximum. This peak's height depends on the thickness of the plasma film and the value of the maximum is largest when $\Gamma_i = \Gamma_r$.

The angular FS spectra shown in figure 2 are obtained as in the above ATR by changing only the angle of incidence in the prism. It is noted that, first, there is a slight shift between maxima in FS and minima in the ATR. This shift is 0.04° at the wavelength 5145 Å, and 0.05° at the wavelength 4965 Å in the work reported here. A similar shift of 0.02° for silver and a larger shift for gold has been reported by Barnes and Sambles (1985). However, one would not expect from the above expressions for reflection or FS intensity these shifts for the peak position for FS from the minimum in ATR, and therefore the values of ε' calculated from the spectra in both methods should be the same. Secondly, one can easily see from figures 1 and 2 that the halfwidths of the ATR inverted

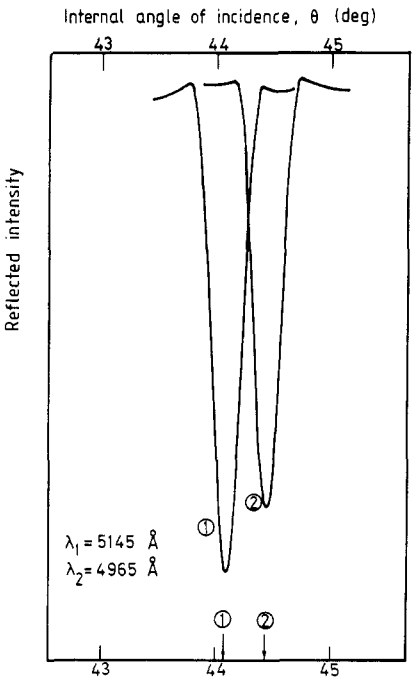

Figure 1. Reflected intensity as a function of angle of incidence θ in the glass prism for two wavelengths (5145 and 4965 Å) as indicated.

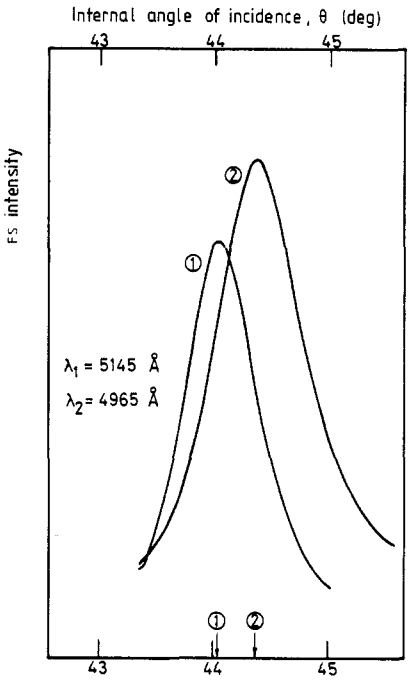

Figure 2. Forward scattered intensity as a function of angle of incidence θ through the prism, collected on the air side of the silver film (the same film as in figure 1) for the two wavelengths indicated.

Lorentzian are different from those of the FS Lorentzian, and that they are two to three times larger in the case of FS. There has been no previous study of such behaviour of the halfwidth, in spite of the fact that the halfwidth in these Lorentzian structure curves is a more sensitive parameter than the position of the angle for maximum coupling, as was noted by Pockrand (1977), since it is indicative of the decay process.

To investigate this change in the halfwidth further, we have also carried out combined PA–ATR angular spectroscopy (Inagaki *et al* 1981, 1982a, b, Talaat and Dardy 1983, Rothenhäusler *et al* 1984, Talaat *et al* 1985). In this case, the metal film sample is enclosed in a PA cell and the detection is done via the heating of the silver film by the non-radiative decay of surface plasmons as well as their interaction with surface roughness. The resonance curve due to the absorption (or non-radiative decay) of surface plasmons in the metal films should follow a Lorentzian shape, as the generated surface plasmon, i.e. the resulting PA–ATR angular spectrum, should follow the same Lorentzian as the ATR. The expression for the signal I_{PA} could then be written as (Rothenhäusler *et al* 1984, Talaat *et al* 1985)

$$I_{PA} = I_0 A(\theta) \tag{5}$$

where $A(\theta)$ measures the conversion of the Lorentzian generated surface plasmon into heat (or sound).

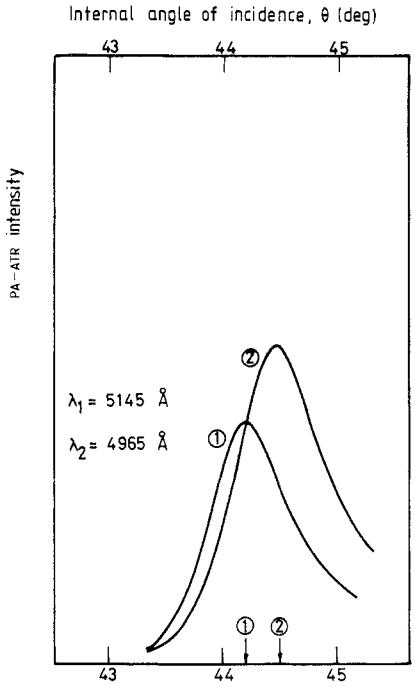

Figure 3. PA–ATR spectra of the same silver film as used to obtain figures 1 and 2 as a function of the angle of incidence θ for the two wavelengths indicated.

Again, the maximum and the halfwidth should be the same as in the other two cases. By carrying out angular PA–ATR spectroscopy for the same Ag film, we obtain the curves shown in figure 3. It is observed that there is a systematic shift between the PA signal and both ATR minima and FS maximum. This shift for PA is always to the right towards larger angles of incidence. Furthermore it is observed that the halfwidths are also larger than the halfwidths in the other two cases, being nearly the sum of the FS and ATR halfwidths. The values of ε', ε'' calculated from the PA–ATR curves are listed in table 1 and show a change from those obtained for FS or ATR.

The difference between the ATR and FS could be understood in terms of the different mechanism involved in the corresponding resonance curves. The ATR minimum shows the response of the system as a whole (Barnes and Sambles 1985), where the inverted Lorentzian in the ATR is a result of the interference between the generated surface (metal/air) modes and the reflected volume (prism/metal) modes. However, as was observed before (Barnes and Sambles 1985), the peak in FS corresponding to the angle of maximum surface charge density may not correspond exactly to the angle of minimum reflection. It also seems that, in our case, the contributions of the surface roughness (natural/surface roughness) to the particular TM polarised modes in the reflection geometry is negligible. On the other hand, the surface roughness that is responsible for the change in the surface plasmon wavevector and hence in the phase velocity of the plasmons, resulting in the generation of the scattered volume modes (or re-radiation), to both the air and prism sides, is more effective in the FS measurements. The effects of this surface roughness are the smaller angle of the FS peak and the enlarged halfwidth in the FS due to the presence of the wavevector components corresponding to surface roughness that causes the scattering of surface modes into volume modes. The peak in the PA–ATR results corresponds to the maximum in the absorption of the generated

surface plasmon at the Ag/air interface which may be different from the angle of maximum surface charge density producing the peak in FS. Also the additional increase in the halfwidth in the case of PA–ATR resonance spectra (in the absence of a complete theoretical calculation of the dissipation of surface plasmons in the PA arrangement) could be explained in terms of an additional decay due to interaction of surface plasmons with surface roughness. While the ATR resonance curve has a halfwidth that includes the intrinsic damping Γ_i and radiation damping Γ_r, the halfwidth for the PA–ATR may include the intrinsic damping and the additional non-radiative damping of the generated surface plasmon by interaction with surface roughness. Hence, this additional increase of the PA–ATR halfwidth over that of the ATR is thought to be of the same magnitude as that of the halfwidth of the FS that is due to interaction of surface plasmons with surface roughness. This may explain the experimental results that show that the halfwidth of the PA–ATR is nearly the sum of the halfwidths of the ATR and the FS. The slight difference of the PA–ATR halfwidth from an exact sum may be due to the complexity of the shape of the PA–ATR resonance spectra, where the Lorentzian generated surface plasmons are dissipated by a Gaussian distribution surface roughness resulting in a convolution of the two spectra, or a Voigt shape. This is under investigation at the present time and will be reported later. To enhance the validity of these arguments, we have carried out the above experiments on Ag films deposited at different rates (0.5–10 Å s^{-1}) to obtain films of varying surface roughness. The resulting resonance curves show that an increase in the surface roughness results in an increase in the shift between the maxima in FS and PA–ATR and the minima in the ATR, as well as an increase in the PA–ATR halfwidth as compared to the FS halfwidth. Finally, it is noted that, since the halfwidth of the resonance curves is a measure of the mean free path of the surface plasmons (Maradudin 1982), it is then a measure of the probability of scattering or absorption of surface plasmons. Therefore, if the additional part of the halfwidth of the PA–ATR that corresponds to the probability of absorption of the surface plasmon by interaction with the surface roughness is of equal magnitude to the halfwidth of FS that corresponds to the scattering of the surface plasmon by the surface roughness, then we may conclude that in our case surface plasmons have an equal probability of being absorbed or scattered into photons. The observation of Rothenhäusler *et al* (1984) that only 25% of the energy absorbed by a surface plasmon is re-emitted by the radiative decay accounted for the radiation on the air side of the Ag film. If the radiation on the prism side were to be included in their calculations, their conclusion could come into agreement with ours.

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