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« SIGNIFICANCE OF SURFACE PLASMONS FOR SURFACE STUDIES »

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**Abstract.** — Radiative and non radiative surface plasmons and their dispersion curves. Excitation of these surface oscillations by electrons and by light. Applications : Sensitivity of the energy of the surface plasmons against surface contaminations. Measurement of surface roughness by means of the plasma radiation. Surface plasmons and reflectivity.

**Introduction.** — In a solid with nearly free electron gas there exist on its boundary oscillations of the density of the surface charges (surface plasmons) besides the oscillations of the volume density of the electrons (volume plasmons). The electric fields of these fluctuating surface charges extend into the interior as well as into the exterior. There are two kinds of modes : see figure 1.

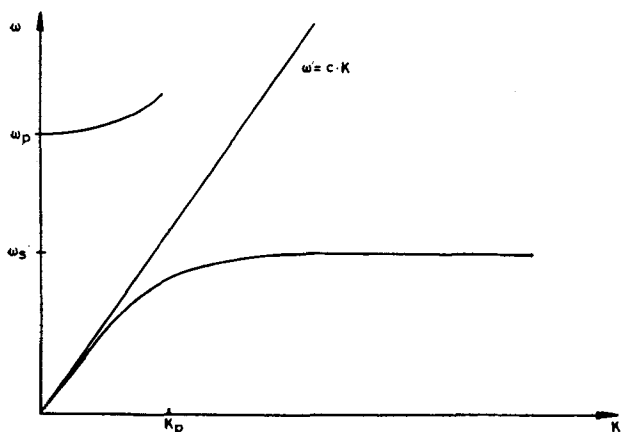


FIG. 1. — Dispersion relation of surface plasmons.  $\omega = c \cdot K$  represents the light line. Left of it one finds the radiative modes, on its right the non radiative ones.  $K_p$  corresponds to  $\omega_p/c$ .

The *radiative* modes : its electric fields outside the plasma have oscillatory character and fulfill the condition  $K < \omega/c$  (predicted by Ferrell). ( $K$  wave vector of the oscillations,  $\omega$  frequency,  $c$  light velocity.) The phase velocity is higher than that of light. The frequency of these oscillations is  $\omega_p$  for  $K \ll K_p$ .

The *non radiative* modes : its fields decay exponentially into the exterior and fulfill the condition

$$K > \omega/c$$

(predicted by Ritchie). The frequency becomes  $\omega_s$  for  $K > K_p$  and goes to zero for  $K < K_p$  due to retardation effects. These modes can be excited by electrons and by light.

1. **Electrons.** — An electron which passes a thin film of a solid transfers a momentum to it and loses the energy  $\Delta E$ . In the case that a volume plasmon is excited,  $\Delta E$  becomes  $\hbar\omega_p$  ( $\omega_p$  plasma frequency) and the transferred momentum that of the volume plasmon. In the case of surface plasmons the transferred energy  $\Delta E$  becomes  $\hbar\omega_s$ ,  $\omega_s$  frequency of the surface plasmon, and its momentum is given by the projection of the transferred momentum on the boundary of the solid :  $\hbar K$ .

The frequency  $\omega_s$  for  $K > K_p$  is given by  $\omega_s = \omega_p (1 + \epsilon)^{-1/2}$  where  $\epsilon$  is the dielectric constant of the boundary medium of the plasma. Its value is thus very sensitive to the nature of this medium. It may be demonstrated here by some experiments which show the displacement and damping of the silver surface plasmons by tarnishing carbon films of known thickness. The positions as well as the half width of the surface loss is changed by the contamination of the surface, whereas the volume loss is not affected. Figure 2 demonstrates this effect clearly and the good agreement between observed and calculated values [1].

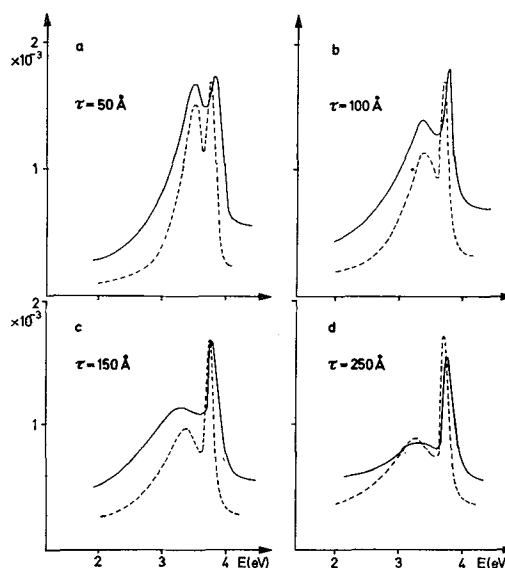


FIG. 2. — Energy loss spectrum of a silver film in transmission with the volume (3,8 eV) and the surface loss (3,6 eV) covered with carbon films of different thicknesses.

A further example of the sensitivity of surface plasmons to surface contaminations is shown by experiments with Al-surfaces, covered with  $Al_2O_3$  films of known thickness [2]. Figure 3a shows the dispersion curve of the surface oscillation without oxide ( $\Delta E = 10.5$  eV) and covered with a very thick oxide film ( $\Delta E \cong 7$  eV). If however the oxyd film has a certain thickness  $\tau$  then great wave lengths of the plasma oscillation (small  $K$  values) are less influenced by this film than small wavelengths. This is demonstrated by figure 3b and c where an oxyd film of thickness  $\tau$  on an Al-surface shows a transition of the 10 eV loss into the 7 eV loss the quicker the greater  $K\tau$ . These experiments are examples for the high sensitivity of the surface plasmons against contaminations.

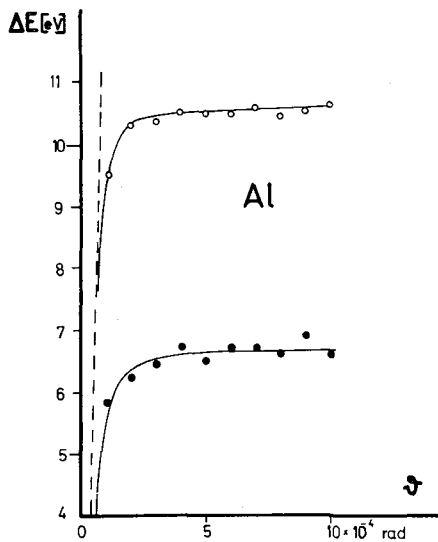


FIG. 3 (a). — Energy loss value of the surface plasmon (without oxyd (10,5 eV) and with a thick oxyd film (7 eV)) as function of the scattering angle  $\vartheta$  or of the wave vector  $K = K_0 \vartheta$  ( $K_0$  wave vector of the incoming electron). Dotted line: light line. At low one observes the retardation effect.

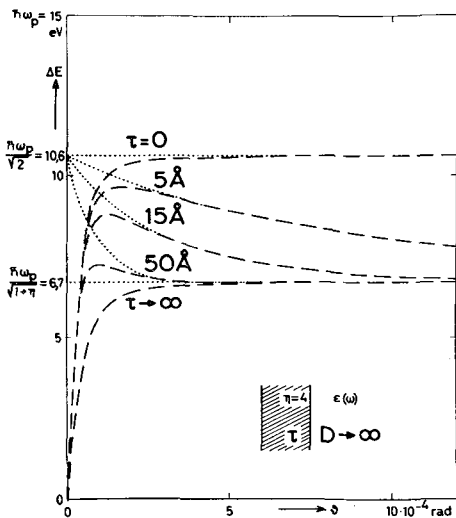


FIG. 3 (b). — Calculated value of the surface loss as function of  $\vartheta$  at different thicknesses  $\tau$  of the oxyd film.

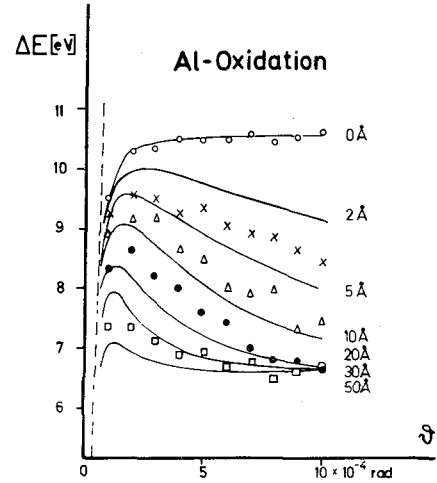


FIG. 3 (c). — Observed thickness « dispersion ».

In the same way the radiative mode can be excited by electrons, its loss energy  $\hbar\omega_p$  is not different from that of the volume loss. The intensity of the surface loss however decreases more rapidly with the scattering angle than the volume loss intensity.

2. **Light.** — **RADIATIVE MODE.** — If one irradiates a surface of a thin film filled with a plasma with light of frequency  $\omega_p$  under an angle  $\theta$ , the component of the light wave vector  $K_l$  along the surface  $K_l \sin \theta$  can excite the radiative mode. This makes a very slight effect in the reflected light, but a strong effect in the transmitted light, well known as plasma resonance absorption [3]. It can be detected by emission too. The interesting point of this plasma resonance emission is that it should not be observed since a smooth surface emits nothing more than the reflected and the transmitted beam. Surface roughness however produces intensity outside of these directions; thus roughness can be determined by this way. This can be explained in the corpuscular conception of light by saying that the plasmon momentum is reduced or increased by a pseudo momentum  $\hbar K_r$ , where  $K_r = 2\pi/\lambda_r$  with  $\lambda_r$  one wavelength of the Fourier spectrum of the surface elevations (Fig. 4). Detailed measurements of the angular

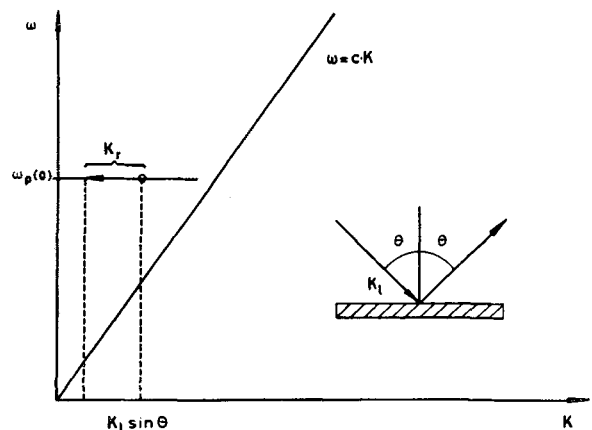


FIG. 4. — Schematic representation of the effect of roughness (given by  $K_r$ ) on the angle of emission of plasma resonance radiation.

distribution of the plasma resonance radiation, frequency dependence, determination of the correlation length of the roughness, etc. could verify the theoretical conceptions [4]. Figure 5 shows as an example the dependence of the emitted intensity of the thickness of the irradiated foil (incidence angle  $30^\circ$ , outgoing angle  $30^\circ$  azimuth  $90^\circ$ ) [5]. The plasma resonance radiation ( $\omega = \omega_p$ ) represents thus a tool for studying surface roughness.

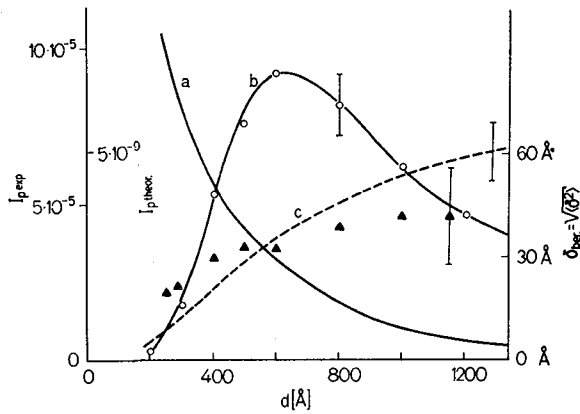


FIG. 5. — The intensity of plasma resonance emission of silver as function of film thickness [5].

NONRADIATIVE MODE. — *a*) It is possible to excite this mode by incoming light of frequency  $\omega < \omega_s$ , and  $K = K_l \sin \theta$  hitting a surface with grating constant  $d$ . It couples with the plasmons reducing its wave vector to  $K_l \sin \theta + 2 \pi/d$ , see figure 6. Backcoupling to  $K_l \sin \theta$  gives an absorption dip

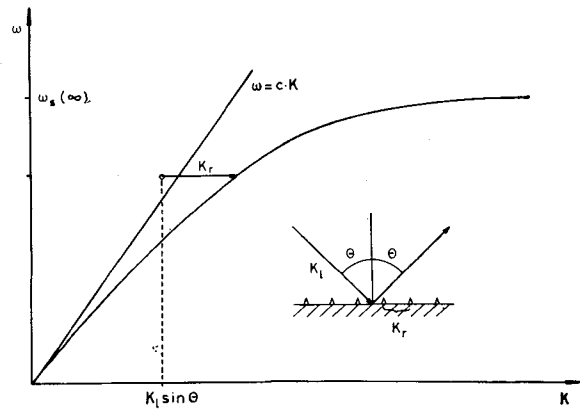


FIG. 6. — Schematic representation of the effect of roughness on the excitation of the non radiative mode by light.

in the reflected beam which is not visible for another  $\theta$  if  $2 \pi/d$  is fixed [6]. This effect produces a change in the reflectivity of light, if it hits a rough surface of a plasma e. g. normally. Figure 7 [7]. The scattered light can be seen in the frequency range  $\omega < \omega_s$ , see figure 8 [8].

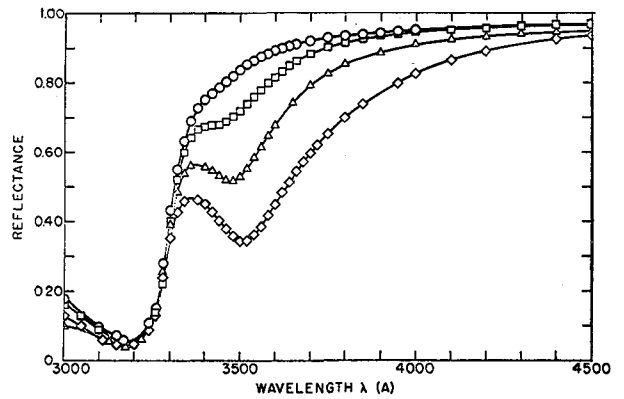


FIG. 7. — Reflectivity of a silver surface (normal incidence) on surfaces of different roughness.

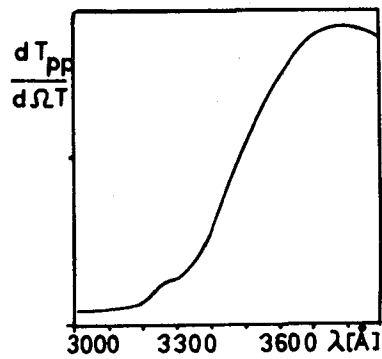


FIG. 8. — Emission of light from a rough silver surface.

*b*) The light momentum can be increased by performing the light experiment in a medium with refractive index  $n > 1$  e. g. glass or quartz, since

$$K = K_l \sin \theta . n .$$

It is thus possible to excite the plasmons in the boundary metal-air. One obtains then a dip in the reflectivity at that frequency and angle  $\theta_n$  where the line  $c/n \sin \theta_n$  crosses the dispersion curve. If these plasmons are coupled by roughness to the left side from the light line one observes light emission. By changing  $\theta_n$  (changing the inclination of the line  $c/n \sin \theta_n$  in figure 9) at a fixed frequency  $\omega$ , with which the

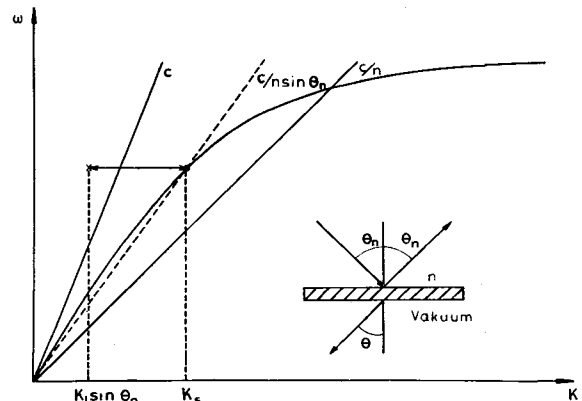


FIG. 9. — Schematic representation of the excitation of non radiative modes by light and reemission of light by roughness.

foil is irradiated, one obtains a strong maximum, if one touches the dispersion curve metal/vacuum [9] (Fig. 10a). As in the case of figure 3b, c where the thickness of the  $\text{Al}_2\text{O}_3$  film is important for the shape of the dispersion curve the thickness of the silver film influences here the dispersion curve of the non radiative plasmons, Fig. 11 [10]. It is in good agreement with theoretical considerations [11]. Further the influence

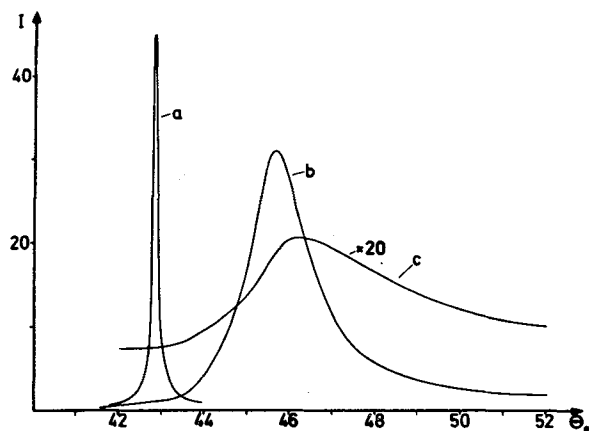


FIG. 10. — Position of the maximum of light emission from non radiative modes of a silver film as function of the angle of incidence  $\theta_n$ . The silver film is covered with carbon films of different thickness : (a) no carbon film, (b)  $\sim 100 \text{ \AA}$ , (c)  $\sim 300 \text{ \AA}$ .

of a contamination here carbon on silver can be seen by the displacement and damping of the radiation maximum (Fig. 10) [10]; see figure 2

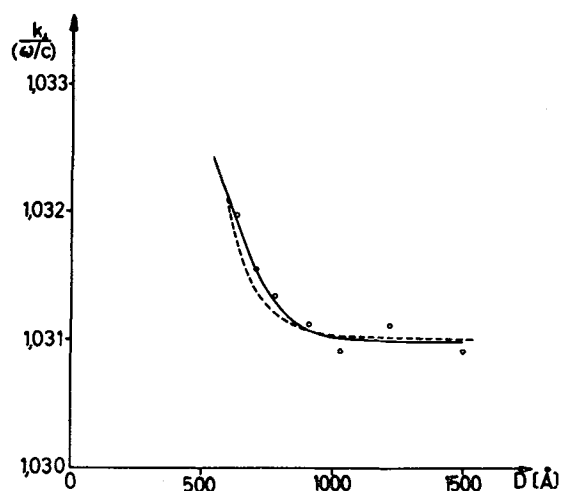


FIG. 11. — Position of the maximum of light emission from non radiative modes as function of the Ag film thickness.

Again roughness studies are possible and since these plasmons are very sensitive to surface contaminations similar experiments as done with electrons can be performed.

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