

## Excitation of Surface Plasma Wave in Layered Structure of Au/Ag Thin Films

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The effective dielectric function of a system consisting of a gold thin film on top of a 50nm silver film on the base of a BK7 90° prism was measured by attenuated total reflection method in visible region. The shift of the dispersion relation of Au-Ag from that of Ag-prism system is found to be proportional linearly to the thickness of Au layer.

## I. INTRODUCTION

Surface plasmon is one of the most important surface mode of excitations which are the counterparts of the excitation of bulk solid, such as plasmons, phonons, excitons, and magnons etc. Surface plasmon on a metal was first predicted to exist by Ritchie,<sup>2</sup> then Ferrell and Stern predicted that a plane polarized beam of light should be able to excite surface plasma oscillation,<sup>3</sup> and later a detailed experiment verified its existence."

Surface plasma wave has, been shown to be a sensitive probe of optical properties of highly reflecting metal films.<sup>5,6</sup> It has been used to probe the coating layers and the roughness of the metal surfaces,<sup>7-10</sup> to study the internal photoemission in a Schottky barrier diode," and to investigate the enhancement in surface enhanced Raman Scattering (SERS).<sup>12-15</sup>

The purpose of this report is to demonstrate the use of surface plasma wave (SPW) to measure the dielectric response function of a very thin metal film with a thickness of less than 100 Å, The SPW is excited by the method of attenuated total reflection (ATR), where a transverse magnetic (TM mode) polarized light is incident upon a lateral surface of a 90° prism, impinging on the prism base from inside with an incident angle greater than the critical angle, so as to generate an evanescent wave which then penetrates the metal films to induce a SPW on the outer surface of the metal film.

In this report the outer layer of thin metal film is Au, and the inner layer of metal is Ag. Au thin film changes the propagation condition of SPW, and produces a shift of SPW resonance position as well as a change of the line shape in the reflectance spectra of prism-metal-air (PMA) system, and the amount of change is proportional linearly to the thickness of Au layer.

## II. THEORY

A surface plasma wave is a transverse magnetic electromagnetic wave associated with a collective mode of motion of electrons at the metal surface, which can travel along the interface of a dielectric and a metal, decreasing in amplitude with distance from the interface. Since SPW is classical in nature, its basic properties may be derived entirely classically.'

For a model in which the interface is assumed to be a sharp geometric plane boundary (Fig. 1a). The electromagnetic fields generated at the interface by the surface mode of

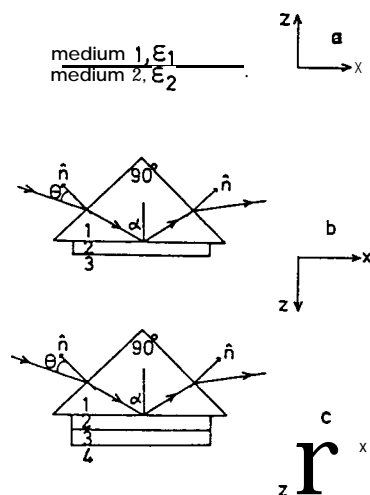


FIG. 1. Geometries of (a) a sharp plane boundary of a metal-dielectric interface; medium 1 is a dielectric with dielectric constant  $\epsilon_1$ , medium 2 is metal with a dielectric function  $\epsilon_2 = \epsilon_2^r + i\epsilon_2^m$ , (b) a prism-metal-air Kretschmann configuration; medium 1 is a prism with  $\epsilon_1$ , medium 2 is a metal layer with  $\epsilon_2$  and medium 3 is air, (c) a prism-metal-metal-air Kretschmann configuration. The prism, metal 1, metal 2, and air are labeled as 1, 2, 3 and 4 respectively. Note that the incident angle  $\alpha$  of the incident light beam to the prism base (i.e. the sample system) is related to the incident angle  $\theta$  to the lateral face by  $\alpha = 45^\circ + \sin^{-1}(\frac{\sin\theta}{n_1})$ .

electrons are determined inside and outside the surface, and the eigenvalue condition which determines the surface modes are obtained by matching the fields inside and outside of the surface. After a detailed calculation by making use of Maxwell's equations, the dispersion relation of SPW is found to be

$$K_{sp}^2 = \frac{\omega^2}{c^2} \frac{\epsilon_1 \epsilon_2(\omega)}{\epsilon_1 + \epsilon_2(\omega)} \quad (1)$$

where  $K_{sp}$  and  $\omega$  are the wave vector and the frequency of SPW respectively,  $\epsilon_1$  is the dielectric constant of air, which will be taken as 1.0 in this report, and  $\epsilon_2(\omega) = \epsilon_2^r + i\epsilon_2^m$  is the dielectric function of the metal, the k-dependence of  $\epsilon_2$  has been neglected for theoretical expediency. Surface plasma waves exist in the frequency region in which  $\epsilon_2^r(\omega) < 1$ . This condition is satisfied for noble metals in the visible light region. Though the

phase velocity of SPW along the interface is of the order of that of electromagnetic waves in the surrounding space, but it remains always less than that of light, therefore, SPW can not couple directly with light in air, i.e. SPW is non-radiative in this model.

However, if a spacer-layer with dielectric constant  $\epsilon_s$  is introduced between the dielectric medium and the metal film such that the dielectric constant of the incident medium,  $\epsilon_1$ , is greater than  $\epsilon_s$ , then the evanescent wave in the spacer-layer could couple to the SPW in the metal film. This method of exciting the non-radiative SPW is called the Otto configuration of ATR method.<sup>16</sup> On the other hand, if a prism is placed close to the metal-air interface to form a prism-metal-air (PMA) system (Fig. 1b), and when TM plane polarized light is incident upon the prism-metal interface at an angle  $\alpha$  greater than the critical angle  $\theta_c$  of the prism, an evanescent electromagnetic wave can also be generated, and which after penetrating through the metal film has a proper parallel component of wave vector  $K_x$  to match with that of surface plasmon,  $K_{sp}$ , so that coupling between SPW and light becomes possible. This way of exciting SPW is called the Kretschmann configuration of ATR method,<sup>17</sup> this is the method adopted in this report.

If Drude model (i.e. for the case of  $\omega\tau \gg 1$ ) is applied

$$\epsilon_2^r(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad (2)$$

where  $\omega_p^2 = \frac{4\pi n e^2}{m^*}$  is the bulk plasma frequency of metal, is used as an approximate dielectric constant for Ag. Eq. (1) can be solved to give a dispersion relation of PMA system for Ag as

$$\omega^2 = K_{sp}^2 c^2 + \frac{\omega_p^2}{2} - \sqrt{K_{sp}^4 c^4 + \frac{\omega_p^4}{4}} \quad (3)$$

When the boundary condition is taken into account for the case of PMA system, and Fresnel's formula is applied, the SPW dispersion relation can be rewritten as<sup>18</sup>

$$K_{sp} = K_0^r + \Delta K_1^r = \frac{\omega}{c} \left[ \left( \frac{|\epsilon_2^r|}{|\epsilon_2^r| - 1} \right)^{1/2} \left[ 1 + \left( \frac{-\epsilon_1^r - a^2}{\epsilon_1^r + a^2} \right) \left( \frac{|\epsilon_2^r|}{|\epsilon_2^r| - 1} \right) e^{-\beta_2 d_2} \right] \right] \quad (4)$$

where  $a^2 = |\epsilon_2|(\epsilon_1 - 1) - \epsilon_1$  and  $\beta_2 = \frac{4\pi|\epsilon_2^r|}{\lambda(|\epsilon_2^r| - 1)^{1/2}}$ , and  $d_2$  is the thickness of metal film. Thus from the wavelength of the incident light and the absorption dip of the reflectance spectra where SPW resonance occurs, one can determine the dielectric function  $\epsilon_2(\omega) = \epsilon_2^r + i\epsilon_2^m$  by Eq. (4) and Kramer-Kronig relation.

If a thin layer of second metal, e.g. Au thin film with  $d_3$  in thickness is deposited on top of Ag film of thickness  $d_2$  to form a prism-metal-metal-air (PMMA) system (Fig. 1c). Under the conditions of  $d_3 \ll d_2$ , and  $|K_{3z} d_3| \ll 1$ , and the magnitude of  $\exp[-2|K_{2z} d_2|] \ll 1$ . that SPW dispersion relation can be rederived as

$$K_{sp} = K_0^r + \Delta K_1^r + \Delta K_2^r \quad (5)$$

where  $K_0^r + \Delta K_1^r$  is the wave vector of SPW in PMX system given by Eq. (4). and

$$\Delta K_2^r = \frac{\omega}{c} \cdot \frac{2\pi d_3}{\lambda} \left[ \left( \frac{|\epsilon_2^r|^{i+1/2}}{|\epsilon_2^r|^{i+1}} \right) \left( \frac{|\epsilon_2^r|}{|\epsilon_2^r|^{i-1}} \right)^2 \right] \left[ |\epsilon_2^r|^{i-1} - 1 + \epsilon_3^r \left( 1 - \frac{|\epsilon_2^r|}{(\epsilon_3^r)^2 + (\epsilon_3^m)^2} \right) \right] \quad (6)$$

$\Delta K_2^r$  is a shift of dispersion relation of the PMA system due to the presence of a second metal film. Eq. (6) has the same form as the result we obtained previously<sup>19</sup> which is valid for a dielectric layer deposited on top of metal film (i.e. PMDA system) and the thickness of dielectric layer is essentially unrestricted, but Eq. (6) derived for PMMA system is valid only when  $d_3 \ll d_2$ . It is seen that the shift of dispersion relation of PMA due to the existence of another thin metal film on top of it is linearly proportional to the thickness of this additional layer, while inversibly proportional to the wave length of the incident light. Thus if one measures the wave vectors of SPW of both PMA and PMMA systems separately, calculate  $\epsilon_2$  for the inner metal film from dispersion relation of PMA system with Eq. (4), then substitute  $\epsilon_2$  and the measured shift of SPW wave vector into Eq. (5), one may obtain a dielectric response function for this very thin metal film.

Since the dielectric response of PMMA system can be regarded as an effective dielectric constant of PMA system, and the variation of which is proportional linearly to the thickness of the outer metal film, the field modification due to the presence of an additional metal film on PMA system is hence expected to be linearly proportional to the thickness of this additional metal film, and therefore the enhancement of radiation field is also expected to be a linear function of the thickness of thin outer metal layer.

### III. EXPERIMENT

High purity Ag (99.999% pure) was first deposited onto the base of a thoroughly cleaned BK70 90° prism by use of an ULVAC EGC-3M electron beam gun in a vacuum chamber maintained at  $2 \times 10^{-7}$  torr, the evaporation rate is controlled at  $> 30 \text{ \AA}/\text{sec}$  to produce a smooth and flat Ag film with a thickness of 500 Å. Then without breaking the vacuum, a very thin layer of Au (99.999% pure) was deposited at a rate of  $\sim 0.5 \text{ \AA}/\text{sec}$  so as to have Au atoms land on the lattice site of Ag. The Au layer was 10 Å, 20 Å, 30 Å, 50 Å, 70 Å, and 100 Å thick for different samples. The samples were then analyzed by Auger spectroscope and electron spectrometer (ESCA). AES profile showed that at the depth of 80 Å the approximate concentration of Au atom is  $\geq 90\%$ , then the Au concentration drops sharply across the Au-Ag boundary at the depth of 100 Å, and decreases further into the Ag film. The appearance of both Au and Ag near both sides of the boundary may be due to the inevitable sputtering of Au atoms into the Ag film during scanning, and due to the inter-diffusion of Au and Ag atoms.

A collimated light beam from Oriel-66188 quartz lamp was sent through a JYH-20 monochromator, polarized by a prism polarizer, then led through a couple of collimating slits to impinge on the lateral face of the prism so as to irradiate the metal film on the base from inside at an incident angle greater than the critical angle. The reflected light beam emerged from the other lateral face of the prism was collected by a RCA-4832 photo-

multiplier tube, signal was then amplified and recorded. When SPW as excited, a sharp absorption dip would appear in the recorded reflectance spectrum, from which the dispersion relation as well as the dielectric function of the system is determined.

#### IV. RESULTS AND DISCUSSION

Figure 2 shows a typical curve of reflectance as a function of incident angle of 5 145 Å light beam, the sharp dip is the position where surface plasma wave was excited. The minimum value of reflectance decreases with increasing the thickness  $d_3$  of Au layer, while

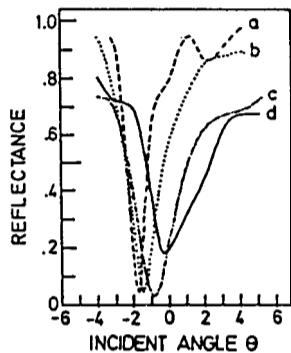


FIG. 2. SPW spectra of prism-Ag-Au-air system as a function of incident angle  $\theta$  when irradiated with 5145 Å light beam. Different curves represent various thickness of Au film deposited on top of a 500 Å thick Ag film: the thickness of Au of curve a is 0 Å, that of curve b is 30 Å, that of curve c is 70 Å, and that of curve d is 100 Å.

the half width of the spectrum increases with increasing  $d_3$ . The reason is that Au is more absorptive than Ag in the whole visible region. The presence of Au would dissipate more of the light to make the dip of reflectance shallow, and lineshape broader.

The phase velocity matching condition of SPW and the attenuated light wave is

$$K_{sp} = \frac{\omega}{c} n_i \sin \alpha \quad (7)$$

where  $n_i$  is the index of refraction of the prism, and  $\alpha$  is the incident angle. Eq. (7) indicates clearly that SPW of larger wave vector would occur at larger incident angle. SPW of Au has a greater wave vector than that of Ag for the same excitation light. Therefore presence of Au will also cause the absorption dip shifted to greater incident angle.

Figure 3 shows the effective dielectric constant  $\epsilon^r$  of the prism-Ag- Au-air system which can be regarded as a modification of the prism-Ag-air system by the presence of Au. The curves are all fallen in between those of pure Ag and pure Au. When  $d_3 = 0$ . i.e.. system reduces to prism-Ag-air, the dielectric constant then agree excellently with the result of Johnson and Christy. When Au is present, and as  $d_3$  increases, the effective dielectric constant curves shift from that of pure Ag toward pure Au regularly, and the amount of

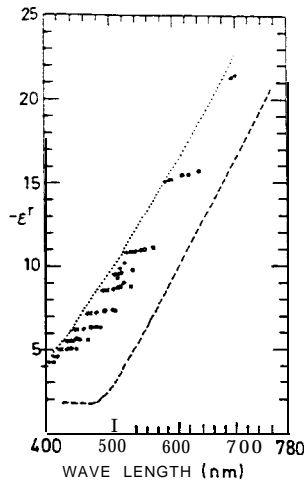


FIG. 3. The effective dielectric constant  $\epsilon'$  of the prism-Ag-Au-air system for various thickness of Au film deposited on top of a 500 Å thick Ag film. The thickness of Au film of the curves represented by mark t is 10 Å, X is 20 Å, o is 30 Å, • is 50 Å, ◊ is 70 Å, • I is 100 Å. The dielectric constants  $\epsilon'$  of pure Ag and Au, reproduced from Ref. (20), are represented by dotted line (Ag) and dashed line (Au).

shift is proportional linearly to  $d_3$ .

Since Ag and Au have same electronic configuration, i.e., their valence band d-orbitals are filled, and s orbitals have a single electron, and they have same density of free electrons, however the optical effective mass of Au is greater than that of Ag, therefore, the binding of valence electrons to Au is greater than that to Ag. Furthermore, the match of lattice constants of Au and Ag is also excellent, in addition there is not a clear cut of the boundary between these two metal films, therefore, the gradual change of the optical property of Ag film in the presence of Au layer is expected. As the effective mass of the PMMA system increases with increasing the amount of Au via increasing the thickness of Au layer, the effective bulk plasma frequency of the system would decrease, and therefore effective dielectric constant decreases as well as can be seen easily from Drude model of  $\epsilon$ . Such a decrease of dielectric constant is equivalent to a shift of the curve of  $\epsilon_r$  versus  $\lambda$  (Fig. 3) from pure Ag toward pure Au. and the addition of a thin layer on top of Ag in the limit  $d_3 \ll d_2$  is effectively the same as distributing Au atom uniformly in the lattice of Ag.

The influence of Au on the dispersion relation of PMMA system is obtained by matching the phase velocity of SPW and the attenuated light wave according to Eq. (7). The measured values of the shift of wave vector of SPW in PMA and PMMA systems is represented by  $\Delta K_2'$  and shown in Fig. 4 as a function of  $d_3$ , as expected, the amount of shift is linearly proportional to  $d_3$ .

The theoretical calculation of  $\Delta K_2'$  according to Eq. (6) is also plotted in the figure as a solid line. The agreement between the experiment and the theory is excellent; the measured  $\Delta K_2'$  deviates from the theoretical value only at large  $d_3$  where the condition  $d_3 \ll d_2$  no longer held as was expected. It is because when  $d_3$  increases to a value not negligible, the SPW will occur mainly in the outer layer, so that  $\Delta K_2'$  will become independent of  $d_3$ . The

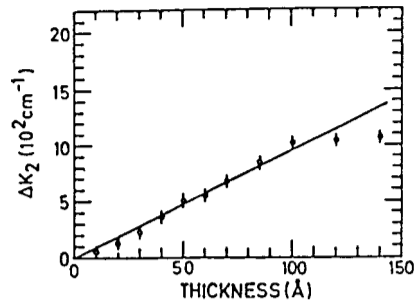


FIG. 4. The shift of wave vector of surface plasma wave as a function of the thickness of Au film deposited on top of a 500 Å thick Ag film, the solid curve is a theoretical calculation of Eq. (7), where dielectric constant of bulk Au has been used.

reflectance spectrum will become shallow and broad to make measurement difficult at large  $d_3$ .

In conclusion, we have measured a linear shift of wave vector of SPW, and the effective dielectric constant of the prism-Ag-Au system in the limit of the thickness of Au layer much smaller than that of Ag. Such results agree very well with theoretical prediction.

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