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Characterization of Berreman modes in metal/dielectric Ag/SiO_2 and Ag/MgF_2 multilayers

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Abstract. The study of Berreman modes, well known in dielectric layers deposited on metallic substrates, is extended in this paper to metal/dielectric multilayers. Infra-red reflectance measurements were performed from 0.05 eV to 0.24 eV under conditions of non-normal-incidence and polarized light incident on Ag/SiO_2 and Ag/MgF_2 multilayers prepared respectively by means of magnetron sputtering and thermal evaporation. Optical ellipsometric measurements were performed in the infra-red on the Ag/SiO_2 multilayers. In the case of p-polarized light, strong absorptions appear, near the longitudinal optical frequencies of SiO_2 and MgF_2, characteristic of the Berreman modes. Other structures were observed in the reflectance and in the ellipsometric parameters at the transverse optical frequencies of SiO_2 and MgF_2. We compare here the results of the two types of optical measurement, and we conclude that photometry and ellipsometry clearly indicate the Berreman modes, ellipsometry giving more information than photometry. We discuss the dependence of these effects on the angle of incidence, the dielectric layer thickness, and the number of periods of the multilayers.

1. Introduction

It is well known that in a metal whose conduction electrons behave like a gas of nearly free electrons, radiative surface modes can be excited at the boundary of the metal by non-normal-incidence light when the electromagnetic wave is p-polarized, i.e. when the electric field has a component perpendicular to the boundary. These surface modes correspond to charge oscillations perpendicular to the interface, and travel along the boundary like guided waves [1, 2]. Non-radiative surface modes, the so-called surface plasmon modes, can also be excited by light in these conditions for certain specific configurations (rough surfaces or attenuated total reflectance (ATR) configurations) [3, 4].

In the case of a metallic thin film, the surface modes at the two interfaces of the film can interact, giving rise to new radiative and non-radiative surface modes [5]. In this paper, we will focus our attention on radiative surface modes of this kind.

These modes appear in the visible or ultra-violet range, near the plasma frequency of the metal, where they produce strong features in the optical response of the metallic thin film for oblique-incidence and p-polarized light.

In the infra-red range, analogous radiative virtual modes have been predicted [6–8] and observed for dielectric or ionic crystal films [9, 10] near their characteristic frequencies,

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ω_T and ω_L (transverse and longitudinal optical frequencies of the bulk material), associated with lattice vibrations.

The modes occurring near the longitudinal optical frequency are usually called Berreman modes. Both modes can be excited with p-polarized light that is obliquely incident, and show up as reflectivity peaks in the optical response. Berreman suggested a configuration allowing an enhancement of the radiative virtual mode at ω_L and reducing the mode at ω_T: the dielectric film is deposited on a metallic substrate or a metallic thick film. The boundary conditions are modified due to the change in the contrast between the dielectric functions of the substrate (previously a dielectric and now a metal) and of the dielectric film. The absorption, proportional to the energy-loss function, is now maximum at ω_L and very weak at ω_T, leading thus to a strong reflectance minimum at the LO frequency and to a faint minimum at the TO frequency [10].

Our interest was in the study of all of these radiative modes in systems where several metallic layers are alternated with dielectric ones. Both electronic modes (in the metal) [11, 12] and ionic modes (in the dielectric) can be observed [12, 13] in this kind of configuration. Effects due to coupling between the modes in each metallic or dielectric layer occur. They have been theoretically studied by calculating [14] the dispersion relations of the coupled modes. The conditions of coupling, depending on the relative thickness of the metallic and dielectric films, vary with the modes which are observed (electronic modes in the UV or visible, ionic modes in the infra-red).

Few results have been published on the Berreman modes in dielectric/dielectric multilayers [15], and to our knowledge we were the first to publish on this effect in metal/dielectric multilayers [12, 13, 15]. Our first experiments were performed only by means of infra-red ellipsometry, and indicated a Berreman mode only at the LO frequency near 0.154 eV in Ag/SiO_2 multilayers. In this paper we extend the study to the three couples of LO and TO modes which can be observed in Ag/SiO_2 multilayers, and to the single couple of LO and TO modes occurring in Ag/MgF_2 multilayers. We have also performed new infra-red measurements by spectrophotometry under oblique-incidence and polarized light that we compare to the ellipsometric measurements.

2. Experiment

2.1. Deposition techniques

The Ag/SiO_2 multilayers were deposited by means of magnetron sputtering under a base pressure of 2×10^{-7} mbar and an argon residual pressure of 5.9 mbar. The diameter of the Ag and SiO_2 targets was 75 mm. The deposition power was around 80 W, and the plasma temperature was lower than 150 °C. The film thickness was deduced from the measurement of a quartz oscillator put in front of the targets in the deposition chamber.

The Ag/MgF_2 multilayers were deposited by thermal evaporation under ultra-high vacuum (10^{-8} mbar). Two tungsten crucibles were used for the deposition, and the mass–thickness of the deposits was measured by two quartz oscillators. A thick film of aluminium was first deposited, during the same experiment, on the glass substrates by using a third source of thermal evaporation.

2.2. Infra-red optical measurements

Two types of optical measurement have been performed on the Ag/SiO_2 multilayers in the infra-red: photometric and ellipsometric measurements. In the case of the Ag/MgF_2

multilayers, only photometric measurements have been performed.

Infra-red optical reflectance (R) measurements with polarized light parallel (p) and perpendicular (s) to the plane of incidence were performed for 45° incidence from 0.05 eV to 0.24 eV using a Perkin–Elmer 580B spectrophotometer equipped with a special attachment for reflectance measurements for non-normal incidence.

Infra-red ellipsometric measurements for 70° incidence were performed from 0.03 eV to 0.5 eV by using an original set-up with rotating polarizers coupled to a commercially available Perkin–Elmer Fourier transform spectrometer. A full description of the system can be found elsewhere [16]. The multiplex advantage of the Fourier transform spectroscopy is utilized to overcome the low-intensity problem in the infra-red.

We have measured the following quantities:

(i) from 0.05 to 0.24 eV: R_p and R_s, the Fresnel intensity reflectance for polarized light respectively parallel and perpendicular to the plane of incidence; and

(ii) from 0.03 to 0.5 eV: $\tan\psi = (R_p/R_s)^{1/2}$ and $\cos\Delta = \cos(\Delta_p - \Delta_s)$, where Δ_p and Δ_s are the phases of the Fresnel reflection amplitudes.

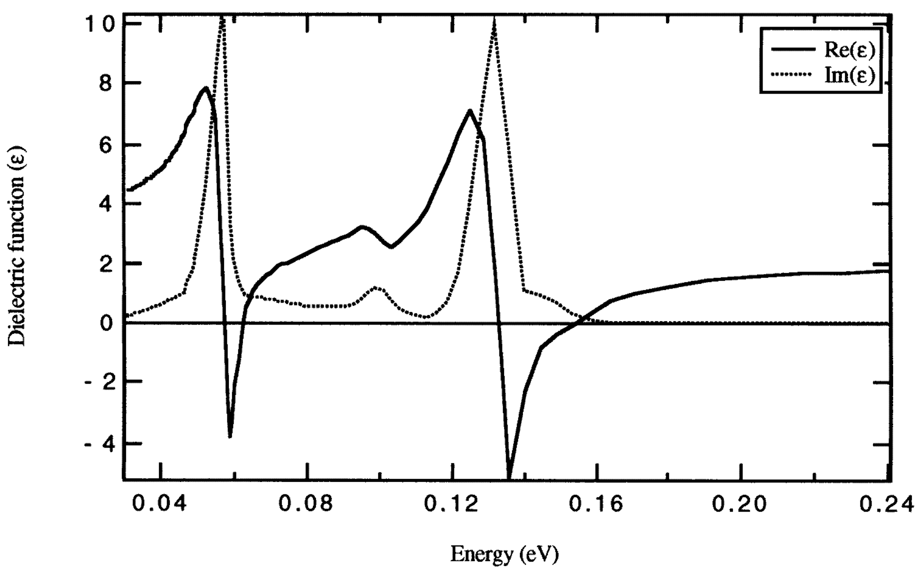


Figure 1. The experimental infra-red dielectric function versus energy for SiO_2 used in the modelling of the Ag/SiO_2 multilayers.

3. Results and interpretation

3.1. Optical modes in pure SiO_2, and MgF_2

The dielectric functions of Ag, SiO_2, and MgF_2 used in our simulations have been deduced from ellipsometric and photometric measurements performed on single layers prepared under the same conditions as the multilayers. The values are in good agreement with the results available in the literature. In particular, the principal characteristic frequencies of the dielectrics are indeed observed at $\omega_{T1} = 0.0568$ eV (460 cm^{-1}), $\omega_{L1} = 0.0625$ eV (500 cm^{-1}), $\omega_{LT2} = 0.10$ eV (800 cm^{-1}), $\omega_{T3} = 0.133$ eV (1070 cm^{-1}), and $\omega_{L3} =$

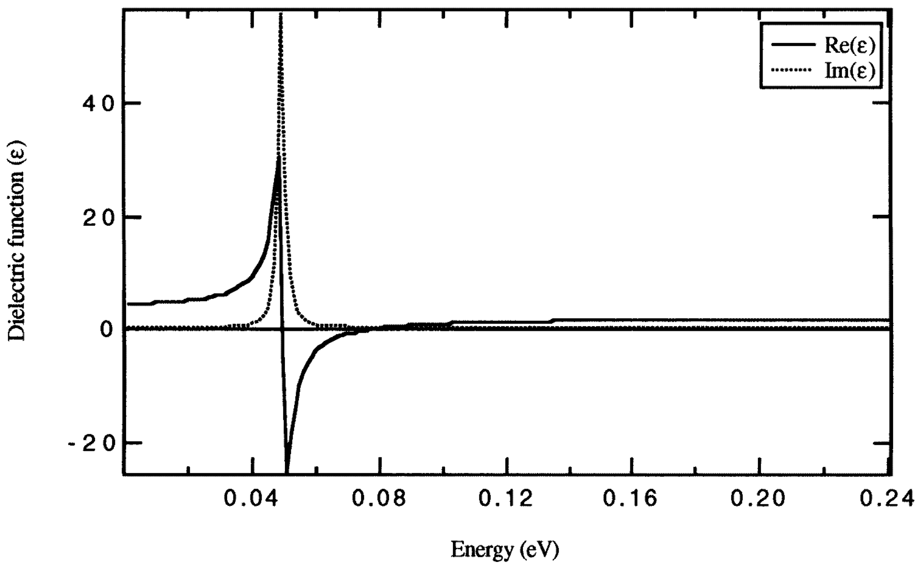


Figure 2. The experimental infra-red dielectric function versus energy for MgF_2 used in the modelling of the Ag/MgF_2 multilayers.

0.154 eV (1240 cm^{-1}) for SiO_2; $\omega_T = 0.051$ eV (410 cm^{-1}), and $\omega_L = 0.078$ eV (630 cm^{-1}) for MgF_2 (see figures 1 and 2).

We recall that the dielectric function of an ionic crystal or a dielectric can be written as a sum of different Lorentz oscillators with the following representation:

$$\varepsilon(\omega) = \varepsilon_\infty \frac{\omega^2 - \omega_L^2}{\omega^2 - \omega_T^2 + \mathrm{i}\gamma\omega}$$

where ω_T and ω_L represent the transverse and longitudinal optical frequencies of the bulk material, ε_∞ is the high-frequency limit, and γ is the damping term.

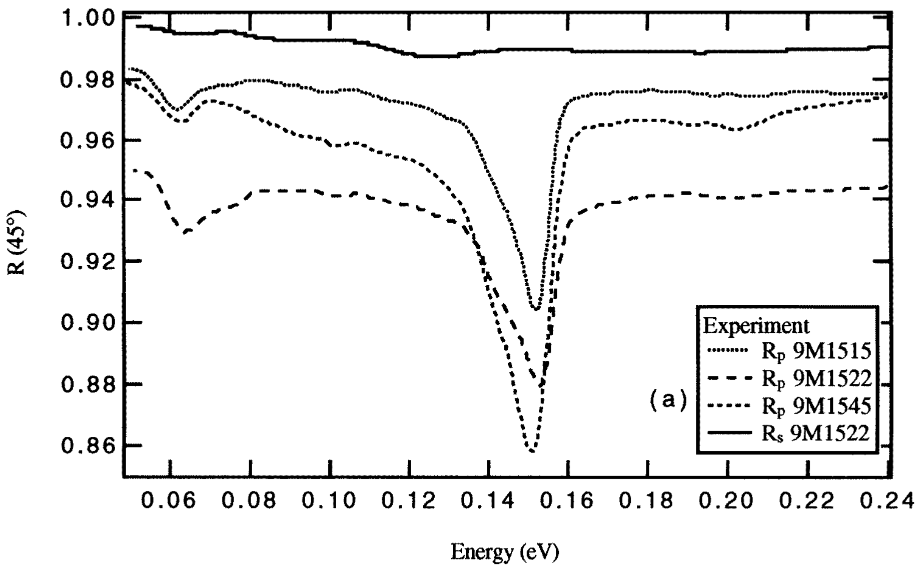
The vibrations associated with the mode occurring near the transverse frequency are parallel to the film surface, while the vibrations associated with the mode occurring near the longitudinal frequency are normal to the film surface.

In the case of pure SiO_2, another mode appears near the characteristic frequency $\omega_{LT2} = 0.10$ eV (800 cm^{-1}). This mode was observed [17] by means of infra-red Raman spectroscopy by Galeener, who interpreted it as being like a mixing between TO and LO modes (‘rocking’ motion).

3.2. Optical modes in Ag/SiO_2 multilayers

The Ag/SiO_2 multilayers which we denote here as 9M1515, 9M1522, and 9M1545 are each composed of nine layers: $SiO_2/Ag/SiO_2/Ag/SiO_2/Ag/SiO_2/Ag/SiO_2$, deposited on glass substrates. In these three multilayers, the Ag layer thickness is 15 nm and the SiO_2 layer thickness is, respectively, 15 nm, 22 nm, and 45 nm.

Figure 3(a) shows the experimental reflectivity measured for 45° incidence for p polarization for the three Ag/SiO_2 multilayers: 9M1515, 9M1522, and 9M1545, and for s polarization for the 9M1522 Ag/SiO_2 multilayer. For p polarization, the reflectivity presents a strong minimum at $\omega_{L3} = 0.154$ eV, characteristic of the Berreman mode associated with



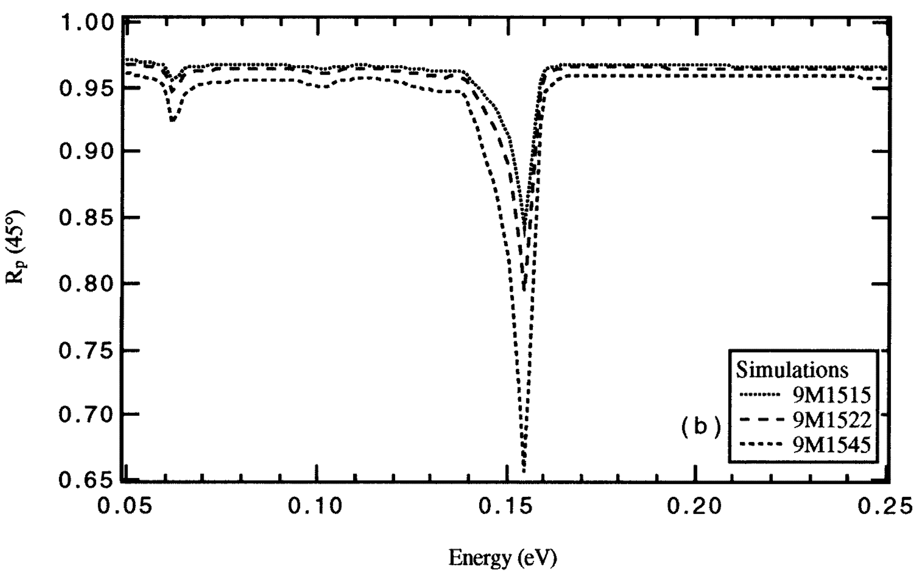


Figure 3. The infra-red reflectance for p-polarized light incident at 45° for three Ag/SiO_2 multilayers each composed of four Ag layers 15 nm thick alternated with five SiO_2 layers 15 nm thick (9M1515), 22 nm thick (9M1522), and 45 nm thick (9M1545), deposited on glass substrates. (a) The experiment, also with reflectance measurements for 9M1522 for s-polarized light. (b) The calculation.

this longitudinal optical frequency of SiO_2. The depth of this minimum depends on the SiO_2 thickness. We also clearly observe the Berreman mode associated with the other longitudinal optical frequency of SiO_2, $\omega_{L1} = 0.0625$ eV. The rocking mode for pure SiO_2 (at around $\omega_{LT2} = 0.10$ eV) does not give rise to an unambiguously observable Berreman mode in these reflectivity measurements on the multilayers. It is only just visible for the 9M1545 multilayer in which the thickness of the dielectric tends towards the optimum thickness for maximizing the Berreman effect [10, 12]. It is more clearly observable in the optical simulations of the reflectivity of these multilayers (see figure 3(b)). These simulations were performed by using the matrix formulation developed for thin single films and multilayers by Abelès [18]. These simulations predict, as usual, sharper resonance peaks than those observed experimentally, because of the influence of the poor quality of the experimental interfaces due to the porosity of the dielectric layers.

The modes in the multilayers, associated with the transverse optical modes in pure SiO_2, appear only, and weakly, for the third mode at $\omega_{T3} = 0.133$ eV in the form of a shoulder in the large peak associated with the LO mode at $\omega_{L3} = 0.154$ eV.

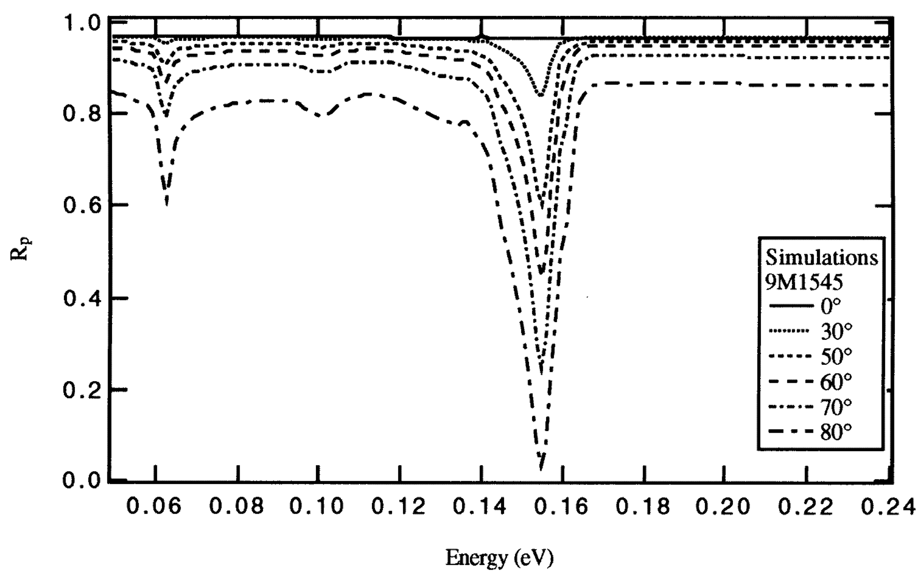


Figure 4. The calculated infra-red reflectance for p-polarized light versus energy for $0^\circ, 30^\circ, 50^\circ, 60^\circ, 70^\circ$, and 80° incidence for Ag/SiO_2 multilayers each composed of four Ag layers 15 nm thick alternated with five SiO_2 layers 45 nm thick (9M1545), deposited on glass substrates.

The visibility of all of these modes, particularly of the weakest ones, can be greatly enhanced by increasing the angle of incidence of the reflectivity measurement. This effect is simulated in figure 4, and shows a huge enhancement at 80°. Unfortunately, our reflectivity measurements were performed only for 45° incidence.

However, the ellipsometric measurements were performed for a higher angle of incidence (70°). Their amplitude component ($\tan\psi = (R_p/R_s)^{1/2}$) (see figure 5(a)) follows strictly the reflectivity response under p polarization (with deeper minima due to the higher angle of incidence), because the reflectivity under s polarization is almost constant and is close to unity (see the R_s-values for 9M1522 in figure 3; 9M1515 and 9M1545 present the same behaviour). It is the phase component of the ellipsometric measurement which provides complementary information in the form of steep edges (see figure 5(b)) at the frequency of the absorptions (reflectivity minima) associated with the different modes. For instance, the weak shoulder in the reflectivity at 0.133 eV clearly shows up in the $\cos\Delta$ measurements.

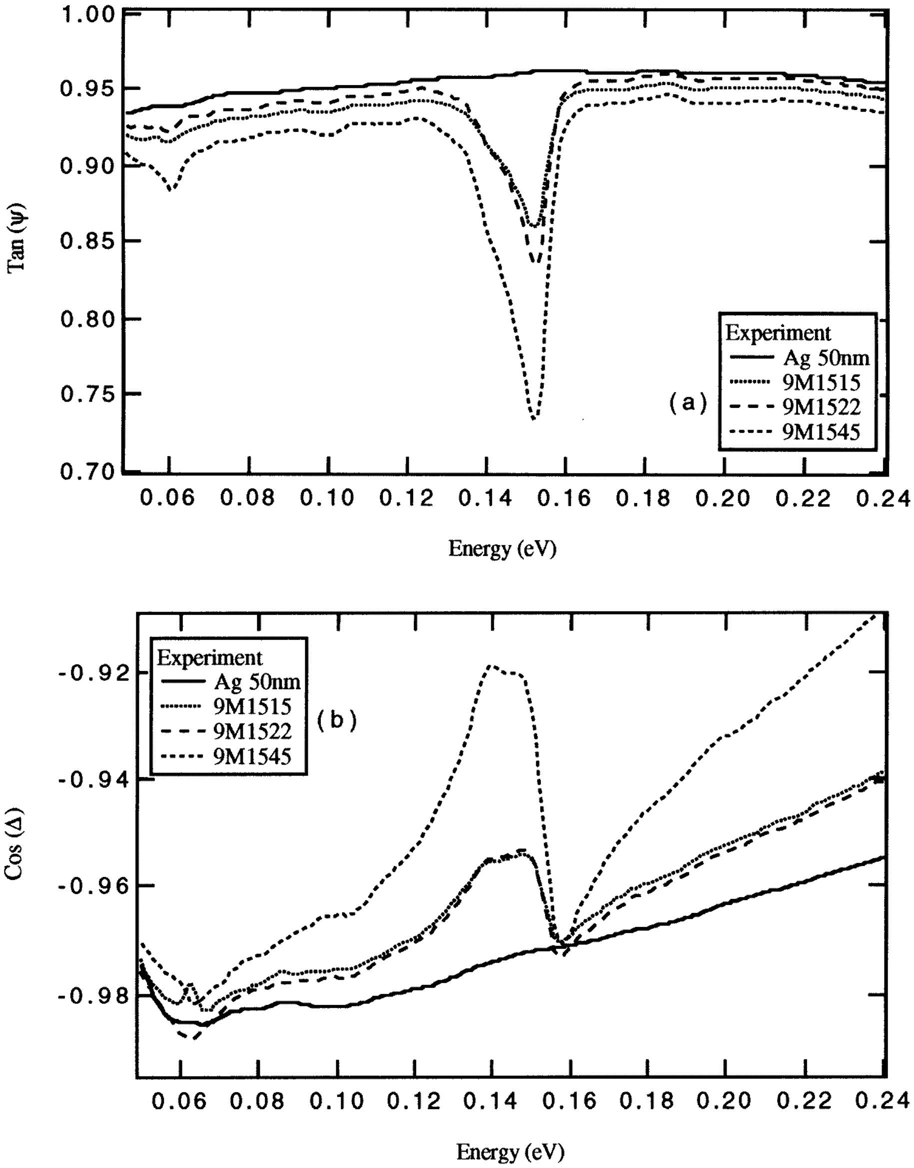


Figure 5. The experimental infra-red ellipsometric parameters $\tan\psi$ (a) and $\cos\Delta$ (b), for 70° incidence, for a Ag monolayer 50 nm thick and for three Ag/SiO_2 multilayers each composed of four Ag layers 15 nm thick alternated with five SiO_2 layers 15 nm thick (9M1515), 22 nm thick (9M1522), and 45 nm thick (9M1545), deposited on glass substrates.

3.3. Optical modes in Ag/MgF_2 multilayers

The Ag/MgF_2 multilayer denoted here as MCAL0401 is also composed of nine layers: MgF_2/Ag/MgF_2/Ag/MgF_2/Ag/MgF_2/Ag/MgF_2, deposited on a glass substrate covered by an Al thick film. The Ag layer thickness is 25 nm, and the MgF_2 layer thickness is 68 nm.

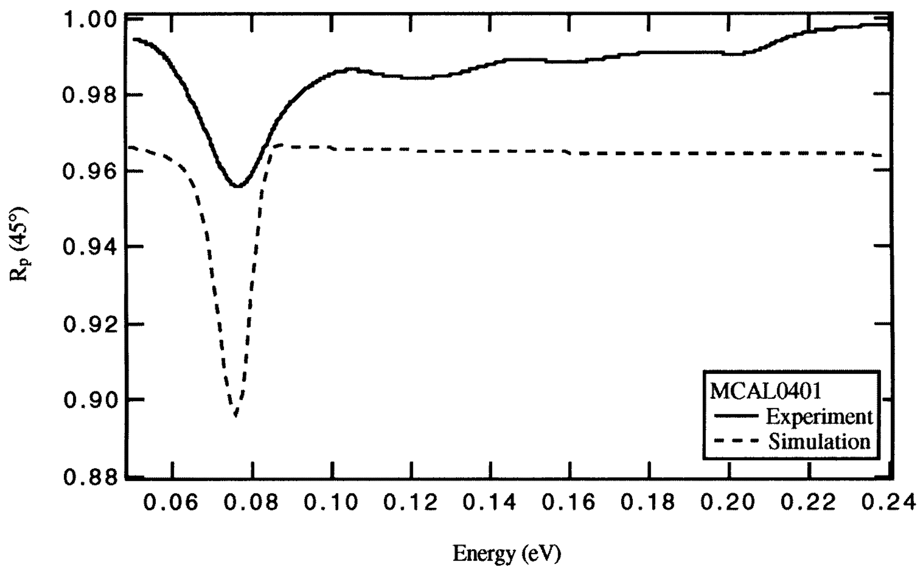


Figure 6. The experimental and calculated infra-red reflectance for p-polarized light versus energy for 45° incidence, for Ag/MgF_2 multilayers each composed of four Ag layers 25 nm thick alternated with five MgF_2 layers 68 nm thick (MCAL0401), deposited on a glass substrate covered by an Al thick film.

Only one oscillator was identified in pure MgF_2 (see figure 2). The Berreman mode associated with the LO mode at $\omega_L = 0.078$ eV clearly shows up in the experimental p reflectivity for 45° incidence (figure 6), in excellent agreement, in energy, with the theoretical calculation (also represented in figure 6); the amplitude has to be corrected for the interface effects as in the previous case of the Ag/SiO_2 multilayers.

3.4. The Berreman effect, and the number of periods in the multilayer

We have shown in a previous paper [12] focused mainly on the optical properties around the plasma frequency of the metal (in the near ultra-violet) that by increasing the number of metal/dielectric periods in the multilayer, one creates coupling effects between the radiative virtual modes, inducing the occurrence of an equivalent number of new radiative virtual modes. In principle, the same effect should occur in the infra-red with the Berreman modes. The experimental results presented above do not show evidence of such an effect. This can be explained by the strong absorption occurring in the infra-red in the metallic layers, even if they are relatively thin, which prevents the coupling. This is indirectly demonstrated by the calculation of the infra-red reflectivity of Ag/SiO_2 multilayers (9M1545 type) with an increasing number of Ag/SiO_2 periods. A difference in the amplitudes of the reflectivity of 3–4% is observed between the responses for one and two periods (figure 7). Then this difference becomes negligible. No new modes show up, thus confirming the absence of coupling between the Berreman modes. This result also shows that one can get the highest reflectivity in the infra-red around the Berreman modes by realizing metal/dielectric multilayers with a limited number of periods (three or four seems to be enough).

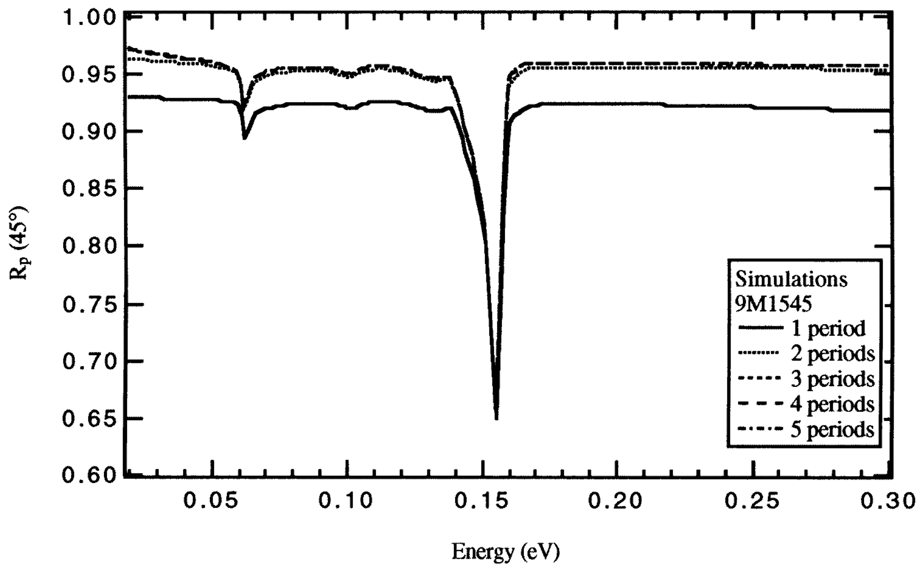


Figure 7. The calculated infra-red reflectance for p-polarized light versus energy for 45° incidence, for a Ag/SiO_2 multilayer composed of a variable number of Ag/SiO_2 period(s) deposited on glass substrates. The Ag layer thickness is 15 nm; the SiO_2 layer thickness is 45 nm.

4. Conclusion

We have observed the three Berreman modes in Ag/SiO_2 multilayers, related to the three LO modes in SiO_2 and the Berreman mode in Ag/MgF_2 multilayers. Ellipsometric measurements have provided an optical characterization of these modes that is more complete and accurate than that provided by classical spectrophotometric measurements, due to the supplementary information contained in the phase of the ellipsometric response.

Unlike for the case of radiative virtual modes observed near the plasma frequency of the metal in the near ultra-violet, we have not observed any effects of coupling between the Berreman modes at the LO frequency of the dielectric in the infra-red. We have attributed this absence of coupling to the strong absorption in the metallic layers in this frequency range.

Acknowledgments

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