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Optical absorption and plasma resonance in very thin films of calcium

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The transmittance and reflectance of very thin films of calcium have been measured at several angles of incidence and for both *s* and *p* polarization, in the energy range 2–5.6 eV. The imaginary part of the complex dielectric constant, ϵ_2, has been calculated making the approximation that the films were thin, plane, and parallel, and the experimental results have been compared with theoretical calculations of Lopez-Rios and Sommers. The interband transitions at 4.4 and 5.1 eV have been confirmed but we found no experimental evidence for that predicted at 2.9 eV. Using obliquely incident *p*-polarized light we have detected a surface plasmon at 3.6 eV, in good agreement with the measurements of energy losses in calcium.

INTRODUCTION

In recent years, a great number of theoretical calculations of the electronic structure of calcium have been performed,[1-3] but experimental results and determinations of the optical constants of this metal are few in number.

Measurements of the reflectance and the transmittance of very thin films of calcium in the energy range 2–5.6 eV have been performed using polarized light at both normal and oblique incidence, and we tried to determine the origin of the structures we observed in the spectra. The imaginary part of the complex dielectric constant ϵ has been calculated from measurements of the reflectance and the transmittance, at normal incidence, assuming plane and parallel films; experimental results have been compared with the corresponding theoretical results of Lopez-Rios and Sommers.[4] For oblique incidence and *p* polarization, an additional absorption appears which might perhaps be due to a plasma oscillation.

APPARATUS AND EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic drawing of the vacuum chamber. The lower part of the chamber consists of a stainless-steel cylinder pumped by an ion pump (1) and a titanium getter pump (2). In the center, there is a molybdenum boat (3) with a movable mask (4). The primary vacuum is obtained by the sorption pumps (6), after which the small ultrahigh-vacuum valve (5) is closed and the ultrahigh vacuum is achieved using the ion pump (1). A pneumatically operated ultrahigh-vacuum valve (7) permits the isolation of the lower part of the apparatus from the measurement chamber. So, during all the experiments, the calcium, contained in the molybdenum boat, is maintained under 8×10^{-10} Torr.

In the ultrahigh-vacuum chamber, which forms the upper part of the apparatus, four suprasil windows (8) are provided which permit the measurement of the transmittance and reflectance of the thin films for both polarizations and for angles of incidence 0°, 45°, and 70°. The plane of polarization is changed by rotating the Glan prism polarizer. The suprasil substrate (9) is positioned in front of the incident beam by means of a slide bar (10). A small ultrahigh-vacuum valve (11) permits the chamber to be connected to the sorption pumps.

To prepare the films, the vacuum chamber is first sealed and pumped down. It is then baked at 200 °C for about 6 h until a pressure of 8×10^{-10} Torr is reached. Calcium of purity 99.9% is carefully degassed several times before evaporation. In the case of barium, another alkaline-earth metal, Bondarenko and Makhov[5] showed that insufficient preliminary degassing has a considerable adverse effect on the structure of the film.

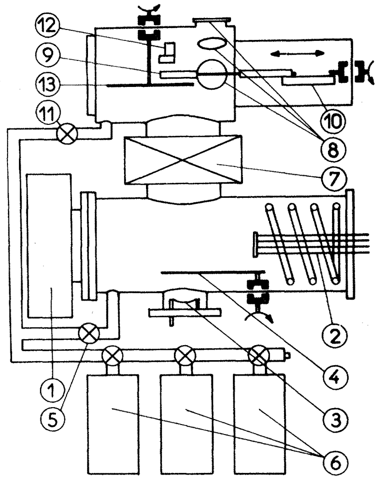

FIG. 1. Schematic drawing of the apparatus.

The calcium is condensed on the suprasil substrate at a rate of 0.4 Å $\sec^{-1}$, the evaporation of metal being detected with a quartz-crystal thickness monitor (12). During the evaporation we use a Talbot disk (13) to obtain simultaneously six thin films of different thicknesses, approximately in arithmetic progression. Part of the substrate is uncoated and is used as a reference during the optical measurements. Great care was taken to ensure identical preparation conditions for all the films in this investigation. Recent works[6, 7] emphasize once again the importance of evaporation conditions in determining film structure.

Since calcium is very reactive, the apparatus was automated in order to reduce as much as possible the time required for our very large number of measurements. The experimental results are recorded on punched tape and computed by means of a program written for an IBM 1130. Repeat measurements of properties at normal incidence were made at the end of each series of measurements so that any drift which might have occurred in film properties could be detected.

EXPERIMENTAL RESULTS AND DISCUSSION

We measured the variations of the transmittance T and the reflectance R of about 60 films with thicknesses varying from 5 to 450 Å approximately. These measurements were made for s- and p-polarized light and for angles of incidence 0°, 45°, and 70°. Figures 2 and 3 present the results obtained for the transmittance versus photon energy $\hbar\omega$ of six typical thin films with thicknesses varying from 35 to 200 Å.

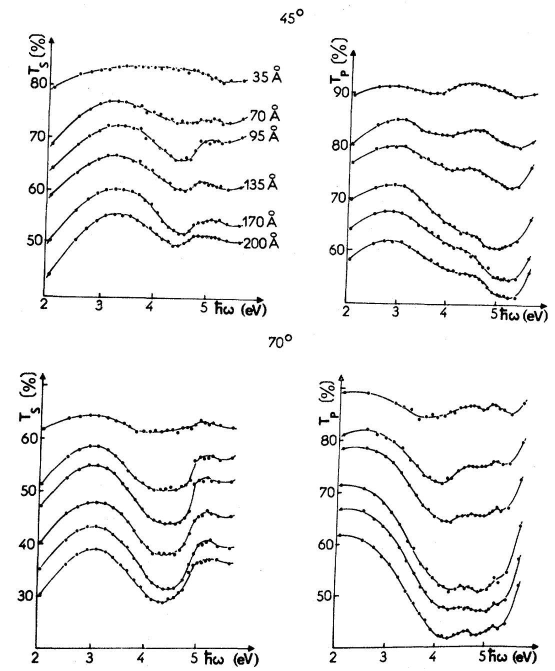

FIG. 3. Variation of the transmittance T, for oblique incidence ($\theta = 45°$ and 70°) and both s and p polarization of the same films studied in normal incidence.

Figure 4 shows the variation of reflectance R for a film 200 Å thick. At normal incidence, the transmittance T shows a minimum at about 5.3 eV. This result is in good agreement with those obtained by Blanc *et al.*[8] under similar conditions.

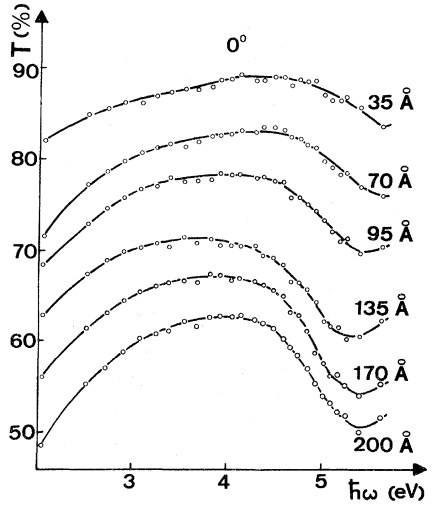

FIG. 2. Variation of the transmittance T, for normal incidence, versus incident photon energy of thin films of calcium of different thicknesses.

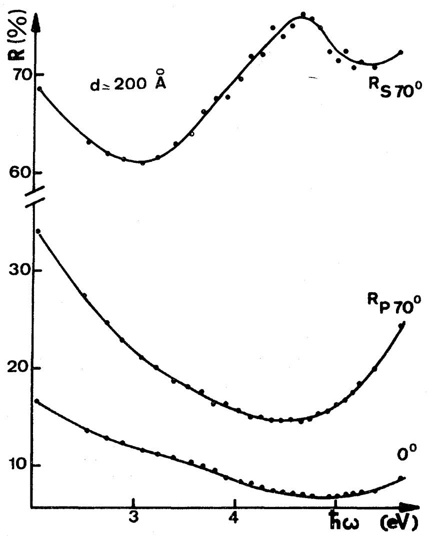

FIG. 4. Variation of the reflectance R of a film 200 Å thick.

The reflectance R, in Fig. 4, shows a minimum at 4.9 eV; Nilsson and Forssell[9] observed such a minimum at 5 eV.

Different authors have given positions for the interband transitions near 5 eV. Particularly, Lopez-Rios and Sommers[4] calculated, from the energy-band plot obtained using a Korringa-Kohn-Rostoker program, the contribution of the interband transitions to the imaginary part ϵ_2 of the complex dielectric constant.

In our case, we calculated ϵ_2 from our experimental results using the relation determinated by Wolter[10] and David[11] for very thin films:

$$\epsilon_2 = \frac{n\lambda}{2\pi d}\,\frac{1-R-T}{T},$$

where n is the substrate index, λ is the wavelength of the incident monochromatic line, and d is the thickness of the film.

On Fig. 5, we can observe good agreement at about 5 eV between the curves deduced from our experimental results and that calculated by Lopez-Rios and Sommers. We find at 5.2 and 4.5 eV the transitions which are theoretically located at 5.1 and 4.4 eV. The peak centered about 5 eV is attributed by Lopez-Rios and Sommers to the d bands falling between 4 and 6 eV above the Fermi level and being nearly flat throughout the zone.

On the other hand, no experimental evidence of the transition theoretically predicted at 2.9 eV has been found and it does not seem to us that this lack of agreement can be attributed simply to the fact that we have been working on thin films.

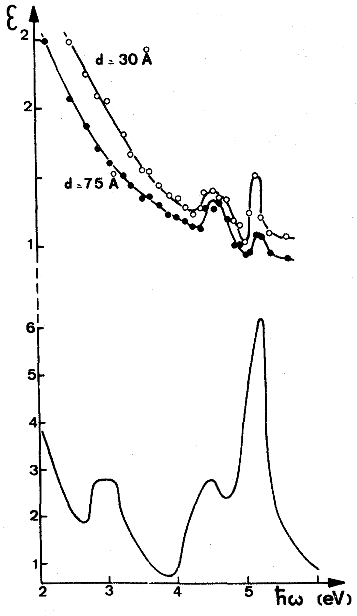

FIG. 5. Variation of $\epsilon_2(\hbar\omega)$ versus incident photon energy for two thin films of calcium (~ 30 and 75 Å). Below is plotted the theoretical curve of Lopez-Rios and Sommers.

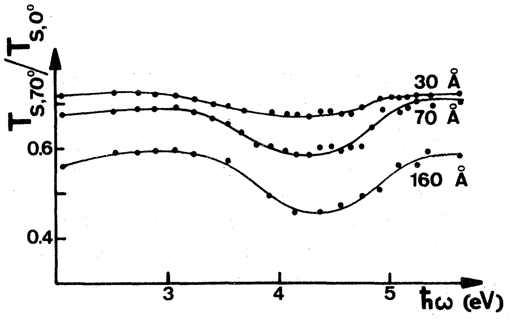

FIG. 6. Variation of $T_{s,70°}/T_0$ vs incident photon energy for films of calcium of different thicknesses.

Also, for normal incidence (Fig. 2), only the interband transition centered at 5.2 eV can be seen on the experimental curve of the transmittance while that centered at 4.4 eV does not appear.

For oblique incidence, the behavior of the transmittance of the deposits is different. For s polarization, a minimum of T_s always exists at 4.4 eV, independent of the angle of incidence. For p polarization, when the electric field $\vec{E}$ is parallel to the plane of incidence and therefore has components both parallel and perpendicular to the plane of the film, another minimum of T_p appears which is more pronounced for greater angles of incidence.

In order to emphasize the effects due to the variation of the angle of incidence for both s and p polarization, we have plotted on Figs. 6 and 7, curves giving the ratio of absolute transmittance T_θ to T_0 for each photon energy (T_θ and T_0 corresponding to the transmittances at angles θ and 0, respectively).

For films of different thicknesses, we find for

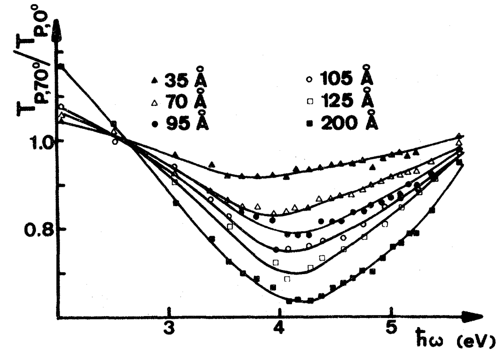

FIG. 7. Variation of $T_{p,70°}/T_0$ vs incident photon energy for films of calcium of different thicknesses.

$T_{s,70^\circ}/T_0$ (Fig. 6) a minimum at 4.4 eV, independent of the thickness of the deposit. While, for $T_{p,70^\circ}/T_0$ the observed minimum shifts towards higher energies with increasing thickness of the deposit (Fig. 7).

It is important to note, first, that this variation of the position of the minimum of T_θ/T_0 can be detected with p polarization only and secondly, that the width of this minimum is greater than 2 eV. The minimum appearing on the curves of T_θ/T_0 (Fig. 6) might be attributed to the effect of an interband absorption because it appears for both polarizations of the incident light, and this is in good agreement with experimental and theoretical results obtained for $\epsilon_2(\hbar\omega)$ which indicate an interband transition at 4.4 eV. With p polarization, the width of the minimum of $T_{p,70^\circ}/T_0$ (Fig. 7) can be explained if we suppose that in addition to the interband transition, another absorption due to a plasma oscillation exists, which broadens the absorption band. This effect occurs at oblique incidence when light polarized parallel to the plane of incidence can exhibit both optical and roughness coupling with surface plasmons.

Raether[12] and Steinmann[13] described different effects of plasma oscillations in the thin films, theoretically predicted especially by Ferrell and Stern[14] and experimentally confirmed by others. Yamaguchi[15] and McAlister and Stern[16] reported similar anomalies of the transmittance of thin silver films, for p polarization of the incident beam. Brambring[17] observed analogous phenomena in potassium films.

In addition, with incident electrons of 40 keV, Schmüser[18] observed a variation with thickness of the energy of the surface plasmon of aluminum at about 6.3 eV, in unsupported films. It is possible to see in Fig. 8 an analogous behavior of our thin calcium films.

Now for a given angle of incidence, it is interesting to examine more closely the way in which the transmittance T differs for parallel and perpendicular components of the electric field. Figure 9 represents the variation of T_p/T_s, when $\theta = 70°$, for a series of films with thicknesses varying from 35 to 450 Å. We can observe two minima, respectively at 3.6 and 5.1 eV, independent of the thickness of the deposit. We note that the magnitude of the minimum at 3.6 eV is greater when the thickness of the films increases.

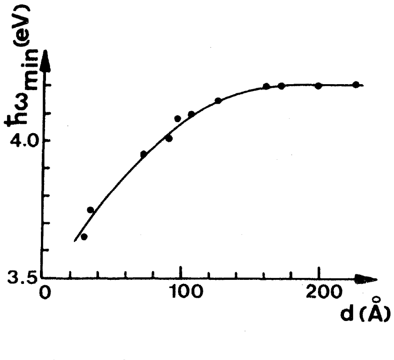

FIG. 8. Value of the abscissa of the minimum of $T_{p,70^\circ}/T_0$ as function of the film thickness d(Å).

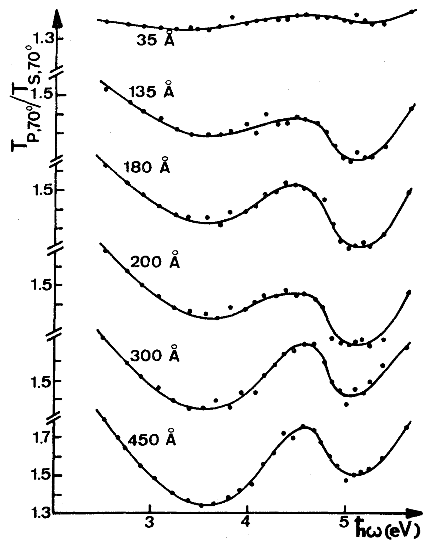

FIG. 9. Variation of T_p/T_s vs incident energy and $\theta = 70°$ for thin films of calcium of different thicknesses.

For the angle of incidence $\theta = 45°$, we have plotted in Fig. 10 curves giving the ratio of absorption A_p/A_s, versus photon energy. We detect two maxima, at 3.7 and 5.2 eV which correspond to the observed minima of Fig. 9. The minimum of

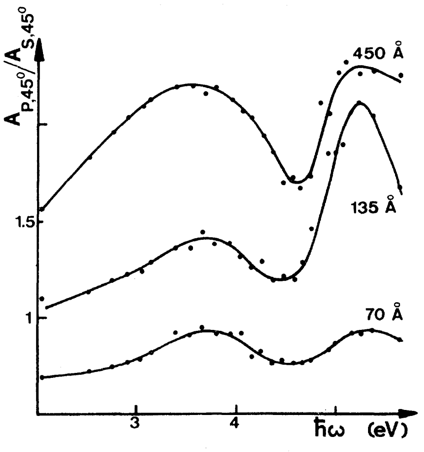

FIG. 10. Variation of A_p/A_s vs incident photon energy and $\theta = 45°$ for thin film of calcium of different thicknesses.

T_p/T_s at 5.1 eV can be compared with that of T for normal incidence and can be attributed to an interband transition, but that at 3.6 eV, which is accentuated when the thickness of films increases, is more likely to be due to a surface plasmon of calcium. Additional evidence is found in the results of Powell,[19] Kunz,[20] Robins and Best[21] who performed measurements of the characteristic electron energy losses in solids and found peaks in the spectra of calcium at 3.7, 4.1, and 3.4 eV, respectively, identified as lowered plasma losses.

We note also that, for a metallic film with a dielectric constant of ϵ, in a medium of dielectric constant ϵ_0, the condition $\epsilon(\omega)+\epsilon_0(\omega)=0$ gives a resonant peak of the surface energy-loss function $\mathrm{Im}\,|1+\epsilon|^{-1}$. Figure 11 gives the variation of $\mathrm{Im}\,|1+\epsilon|^{-1}$ versus incident photon energy, calculated from the complex refractive index of calcium, $n-ik$, using the values determined, with a Kramers-Krönig analysis, by Potter and Green.[22] The resonant peak of this function, located at 3.6 eV for calcium, corresponds to a surface-plasma absorption and is in good agreement with our experimental results.

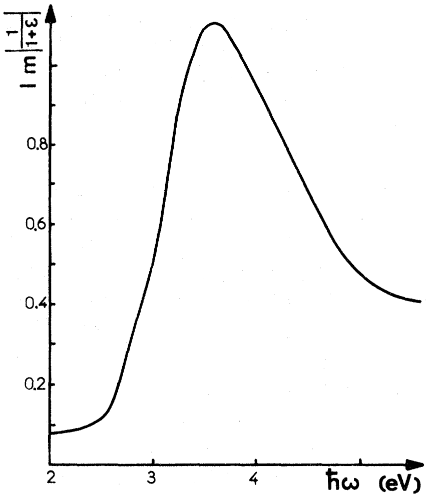

FIG. 11. Surface-energy-loss function $\mathrm{Im}\,|1+\epsilon|^{-1}$ vs incident photon energy from the results given by Potter and Green.

CONCLUSION

In conclusion, this experimental study of very thin films of calcium, in polarized light at normal and oblique incidence, confirms the d-band transitions of 4.4 and 5.1 eV, predicted by Lopez-Rios and Sommers. But there is no experimental evidence of the theoretical transition predicted at 2.9 eV.

The additional absorption band detected at 3.6 eV, with p polarization and oblique incident light, is probably due to absorption by a surface plasmon, and compares well with the results of electron energy losses in calcium obtained by several workers.

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