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FREE ELECTRON ANALYSIS OF THE OPTICAL PROPERTIES OF THERMAL EVAPORATED GOLD FILMS

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Abstract

Gold films of thickness 150-300 Å have been deposited on quartz substrates using vacuum evaporation technique. Spectrophotometric measurements of transmission T and reflection R at normal incidence have been carried out in the range 0.4 – 3.0 μm. The real and imaginary parts of the complex refractive index n have been determined using a developed algorithm based on Murmann's exact equations. The accuracy in the determined n and k was found to be ± 6.0% and ± 1.6%, respectively. The dispersion curve of n showed an anomalous dispersion in the visible region characterized by a peak at $\lambda = 0.840$ μm. The dielectric constants have been calculated and presented. The Drude model parameters ω_p and ω_τ and the d.c. conductivity have been determined and compared. The results showed that such parameters could be obtained from free-electron analysis for the near IR experimental results and the intraband transition contribute significantly to the dielectric functions.

Introduction

The dispersion formula for intraband transition, as established by Drude [1], treated the conduction electrons as free particles of mass m and charge e. The particles are accelerated by the electric field associated with the incident wave and damped by force proportional to their velocity, which is also responsible for their finite conductivity.

Drude model is characterized by two parameters namely, ω_p and ω_τ which are the plasma frequency of collective oscillations of the free electrons and the damping frequency, respectively. It was seen from earliest investigations that Drude's free-electron theory failed in the visible and ultraviolet regions. In the noble metals, free-electron effects are dominant in IR region [2]. The interaband contribution to the dielectric constants can therefore, be separated from the interband contribution by determining values for ω_p and ω_τ . On the other hand, Parkins et al. [3] showed that even the noble metals in the IR can have small interband contributions to the dielectric constants.

The most earlier determination of the dielectric constants as deduced from the optical constants are similar in their spectral behaviour but disagree to their actual magnitude. Such disagreement is due to the problems of sample preparation, accuracy of measurements and method of determining the optical constants. In this regard, Drude model, if it is appropriate, provides a useful parameterization for the optical constants data.

Bennet et al. [4] reported that the Drude model fits the measured reflectance of gold, silver and aluminium in the 3-30 μm wavelength range with one adjustable parameter, i.e. The Drude model parameters were obtained from d.c. conductivity and fitted with one free electron per atom for gold and silver. Also it has been shown that [5] the Drude model provides a good fit for gold with no adjustable parameters in the far IR (66.7 μm to 318 μm).

Ordal et al. [6,7] calculated ω_p and ω_τ which produced the curve with the best eyeball fit to the published experimental data, i.e., the values of ω_p and ω_τ obtained from the far IR data were changed by trial and error eyeball technique to obtain curves most closely matching the experimental data of ε_1 and ε_2 . Also Ordal et al. [8] obtained values for the dielectric constants at submillimeter wavelengths using Kramer-Korning analysis of the normalized surface resistance determined from the non-resonant cavity measurements. They used a spline fit to bridge the data and they reported values for ω_τ and ω_p .

In this regard, it is worthy to note that such fitting techniques give reasonable estimate for ε_1 but not for ε_2. In addition, the presence of band structure combined with a lack of far IR data, limit the Drude model fit to a fairly narrow wavelength range (e.g., Ti).

Several investigations of gold have used the Kramers-Kronig technique applied to normal-incidence reflection measurement . A problem of this method arises from the necessity of extrapolating the reflectance to frequencies outside the measured range. The choice of the extrapolation has a large effect on the magnitude of the optical constants, although the photon energies at which various structural features occur are insensitive to it.

In the present work, the optical constants, n and k, have been accurately determined from spectrophotometric measurements of R and T. A developed computing technique [9] based on the Murmann's exact equations have been used. The dielectric constants, ε_1 and ε_2 have been calculated since they are closely related to the electronic structure of the solid and can be more directly compared with the theory. The free-electron analysis have been performed in the near IR from 0.4 – 3 µm. Determination of the Drude model parameters have been carried out and the results are compared with those obtained through fitting techniques.

2. Sample preparation and results

Gold films have been deposited on quartz substrates by thermal evaporation under vacuum better than 10^{-5} mm Hg. The substrates were cleaned ultrasonically and were dried by hot air. The substrates were masked until the source reached the evaporation temperature and the rate of evaporation was made fast ~ 75 Å S^{-1} to ensure the surface smoothness of the films. The thickness of the films ranged from 150 to 300Å as determined in-situate by a quartz thickness monitor. The transmission T and reflection R for light incident normally were measured at room temperature using a double beam spectrophotometer, UV-3101PC; Shimadzu. The values of R and T were corrected for reflection from the substrate surface. Fig. (1) shows the spectral behavior of the corrected values of T and R for films of different thicknesses. All films show high IR-reflectance increasing with film thickness. The curves show also transmittance peak in the visible range which became more defined at higher film thickness.

The refractive index n and the extinction index k have been determined over he spectral range from 0.4 to 3.0 μm with 0.005 μm wavelength step. The used method was previously explained [9] which is based on the Murmann's exact equations. Figs. (2) and (3), solid lines, show the spectral variation obtained experimentally of the n and k, respectively. These values are averaged for several films. The height of the arrows represents the estimated error in calculating n and k. Both errors grow smaller towards the shorter wavelength. Fig. (2) indicates that the refractive index n exhibits anomalous dispersion in the visible region like other nobel metals [10]. Data given by other authors are represented for comparison [8, 11-13). It is clear that the spectral behavior of both n and k agrees with one another while the same differences appear, as expected, between the absolute values, particularly in the n values. The real and imaginary parts of the dielectric function have been calculated and given in table 1. It is to be noted that the values of n are small, in the IR region, while those of k are large. Accordingly the calculated values of ε_1 are relatively more accurate than those of ε_2 since the former is K^2 while the latter is equal 2 nk.

3. Determination of the Drude Model Parameters

If n and k are the real and imaginary parts of the complex refractive index n, then Drude theory yields the following expressions

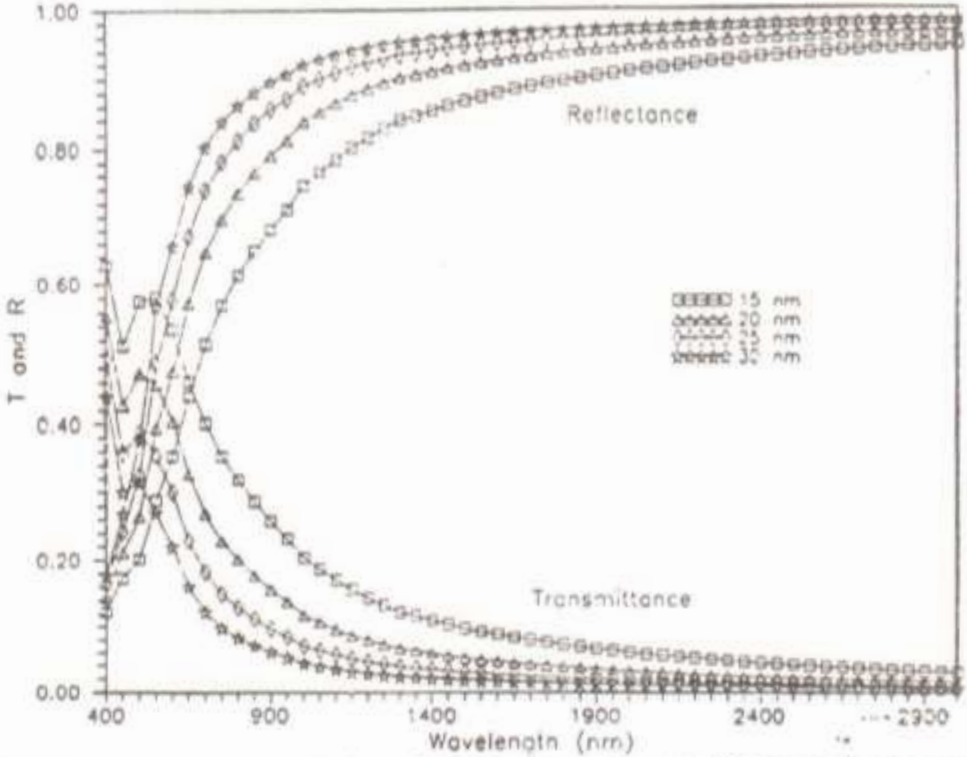

Fig. (1): Spectral variation of trnasmittance T and relfectance R of gold films.

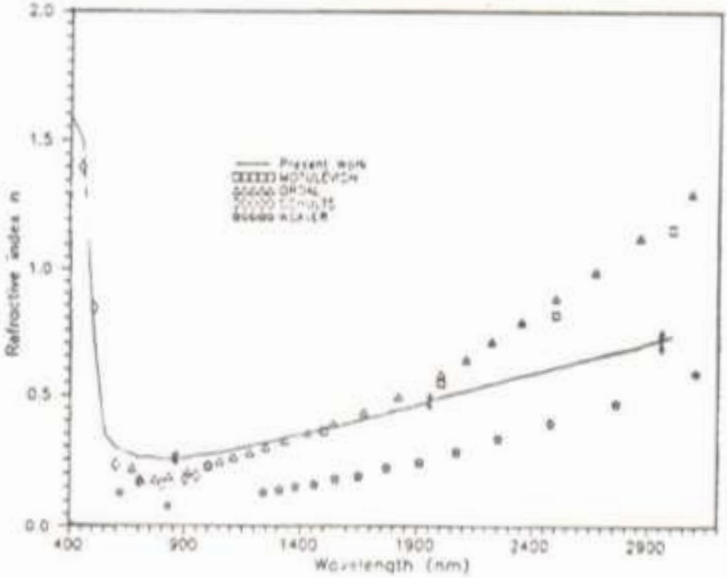

Fig. (2): Spectral variation of the refractive index n.

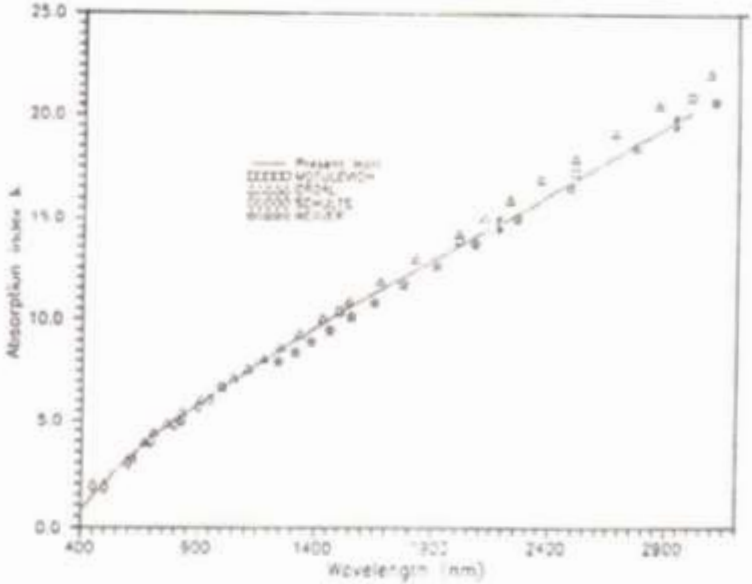

Fig. (3) Spectral variatioin of the absorption index k.

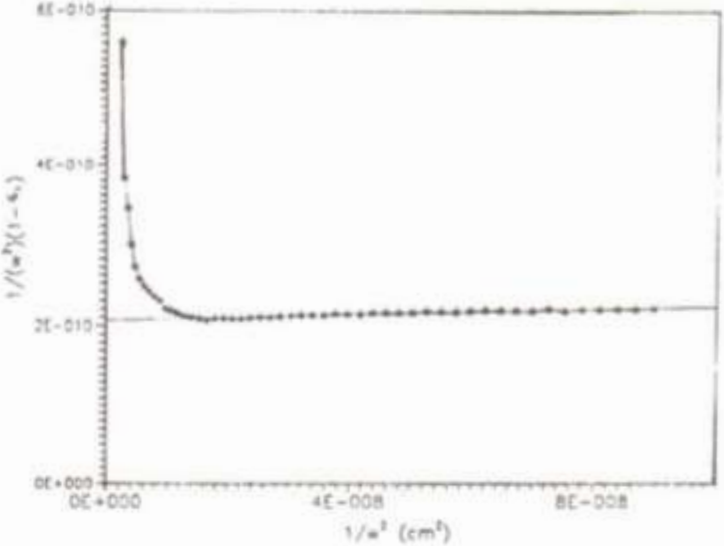

Fig. (4) Plot of $[\omega^2(1-\varepsilon_1)]^{-1}$ vs $1/\omega^2$

for the dielectric functions;

$$\varepsilon = \varepsilon_1 + \varepsilon_2 = (n + ik)^2 = \varepsilon_{oo} - \frac{\omega_p^2}{\omega^2 + \omega\,\omega_\tau} \qquad (2)$$

where ε_{∞} is the high frequency dielectric constant, ω_p and ω_τ are the plasma and damping frequencies expressed in cm^{-1}.

Separating real and imaginary parts we get the known expressions for the dielectric function ω_1 and ω_2 in terms of the Drud's parameters ω_p and ω_τ. Solving such equations for ω_p we get.

$$\omega_\tau = \frac{\omega\varepsilon_2}{1-\varepsilon_1} \text{ then } \omega_p^2 = (1 - \varepsilon_1)(\omega + \omega_\tau^2) \qquad (2)$$

The last two equation were used previously to calculate the lowest frequency (far IR) data for ω_τ and ω_p [6-8] then changed through ε_1 and ε_2 by trial and error to obtain curves most closely matching the experimental data for ε_1 and ε_2 in both behavior and magnitude.

In this work the Drude parameters have been determined directly from the results obtained experimentally for the optical constants n and k as follows.

Rearranging the terms in equations for ε_1 we get

$$\frac{1}{\omega^2}\,\frac{1}{(1-\varepsilon_1)} = \frac{\omega_\tau^2}{\omega_p^2}\,\frac{1}{\omega^2} + \frac{1}{\omega_p^2} \qquad (3)$$

The last equation shows that the plot of $1/\omega^2\,(1-\varepsilon_1)$ vs $1/\omega^2$ is linear as required by free-electron theory. The Drude model parameters are obtained form the slope of the straight line and its intercept with the ordinate.

Fig. (4) shows a plot of $1/\omega^2\ (1-\varepsilon_1)$ vs $1/\omega^2$ based on the determined values of n and k obtained experimentally. It is clear that for $\lambda > 1.2\ \mu m$, a linear relation resulted as required by the free electron theory. Thus, it is clear that for $\lambda > 1.2\ \mu m$ intraband transition contributes significantly throughout the spectral range investigated in this work. This means that the free-electron behaviour dominates in the near IR where n is small and k is large. From the intercept at the ordinate, the plasma frequency ω_p was calculated and found to be $6.69 \times 10^4\ cm^{-1}$ whereas from its slope, the damping frequency was found to be $2.92 \times 10^2\ cm^{-1}$. Comparison between the present results and those obtained by other authors through fitting techniques is given in table (2). It is clear that our values are more adjacent to the values reported recently and obtained by analysis of non-resonant cavity measurements of surface resistance.

Table (2) : Results of Drude model parameters for gold

Author	$\omega_\tau\ (cm^{-1})$	$\omega_p\ (cm^{-1})$
Ordal et al. [6,7] using far IR fit	2.15×10^2	7.28×10^4
Ordal et al.[8] using surface resistance fit at submillimeter range	2.00×10^2	7.25×10^4
Present work	2.92×10^2	6.97×10^4

The high frequency optical conductivity σ_{opt} is related to ω_p and σ_τ by relation [7].

$$\sigma_{opt}\,(\mathrm{cm}^{-1}) = \frac{\omega_p^2}{4\pi\,\omega_\tau} = \frac{9 \times 10^{11}}{2\pi c\,[\rho_{opt}(\mathrm{r\ cm})]} \qquad (5)$$

Substituting for ω_p and ω_τ yielded the optical resistivity: $\rho_{opt} = 3.6 \times 10^{-6}\ \Omega\mathrm{cm}$. This value is slightly higher than the d.c. resistivity given in text books for bulk, namely, $\rho_o = 2.44 \times 10^{-6}\ \Omega$ cm. It is to be noted that our value had been obtained for films, d = 200 Å, which is not necessarily representing the bulk.

The optical mass m_o and the relaxation time τ are related to the Drude's parameters by the relations.

$$\omega_p^2 = \frac{4\pi N e^2}{m_o} \quad \text{and} \quad \omega_\tau = \frac{1}{2\pi c \tau} \qquad (6)$$

where N is the density of the conduction electrons. Substituting for $\omega_p = 6.69 \times 10^4\ \mathrm{cm}^{-1}$ and $\omega_\tau = 2.92 \times 10^2\ \mathrm{cm}^{-1}$, we get $m_o = 10.3 \times 10^{-27}$ gm = 1.1 m_e and $\tau = 18 \times 10^{-15}$ sec.

4. Conclusion

The optical constants of thermally evaporated gold films are presented over the spectral range from 0.4 – 3.0 µm. Free electron analysis showed that intraband transition contribute significantly to the dielectric constants. The Drude model parameters could be successfully obtained directly from the near IR data, i.e., the calculated values are in good agreement with those determined through fitting techniques of data obtained by either far IR or normalized surface resistance measurements.

5. References

1. Wooten, F., Optical Properties of Solids (Aca, N.Y., 1972). P. 52.
2. Johnson, P. B. and Christy, R. W Phys. Rev. B 6, 4370 (1972).
3. Parains, G. R., Lawrence, W. E. and Christy, R. W., Phys. Rev. B 23, 6408 (1981).

4. Bennet, H. E. and Bennet, J. M. in Optical Properties and Electronic Structure of Metals and Alloys F. Abeles, Ed. (North-Holland, Amster. Wiley, N.Y., 1966), Sec. II. 6, P. 175.
5. Brandi, G. and Sievers, A.J., Phys. Rev. B 5, 3550 (1972)
6. Ordal, M. A. Long, R.W. and Ward, C. A., Appl Optics, Vol 22,No. 7 1099 (1983).
7. Ordal, M. A., Bell, R. J., Alexander, Jr., R. W., Long, I. I and Querry, M. R., Appl. Optics, vol. 24, No. 24, 4493 (1985)
8. Ordal, M. A., Bell, R. J., Alxander, Jr., R. W., Long, I. I., and Querry, M.R., Appl. Optics, vol. 26, No. 4, 744 (1987).
9. M. M. El-Nahass, H.S. Soliman, N. El-Kadry, A.Y. Morsy and S Yaghmour, J. Mat. Sci. Lett., 1050 (1988).
10. El-Kadry, N. and kaid, F., Egypt, J. Sol., Vol. 15, No. 1, 9 (1992)
11. Scultz, L. G., J. Opt. Soc. Am. 44, 356 (1954).
12. Motulevich, g. P., and Shubin, A.A., Sov. Phys. JETP 20, 560 (1965).
13. Weaver, T. H., Krafka, C., Lnch, D. W. and Koch, E. E., Physics Data, Optical Properties of Metals, Fachin formation Zentrum, karl Sruhe, FRG, (1981).

Plate (1)

Plate (2)