Quantum Size Effect in Optical Spectra of Thin Metallic Films

J. Dryzek and A. Czapla
Department of Solid State Physics, Academy of Mining and Metallurgy (AGH), 30-059 Krakow, Poland
(Received 14 April 1986)

We test the influence of the quantum size effect on the optical transmission and reflection spectra of films of free-electron metals. We have made measurements on sputtered gold films of thicknesses less than 6 nm. The agreement between theoretical and experimental dependences provides qualitative support for the quantum-size-effect origin of the observed deviation from the classical model.

PACS numbers: 73.60.Aq, 78.20.Dj, 78.65.Ez

If the thickness of a film of free-electron metal (FEM, i.e., simple metals, such as sodium, and Au, Ag, and Cu) is comparable to the mean free path of the electrons, an anomalous behavior of its optical properties appears. This is due to both the classical (CSE) and the quantum (QSE) size effects. The case of CSE has been treated before.[1-3] The aim of this work is to examine the optical characteristics of FEM films with the QSE taken into account. We show that the QSE supplies some novel features in the optical spectra of very thin metallic films.

In our consideration we will admit that for the optical properties in thin FEM films the most important point is the discreteness of the energy levels resulting from the geometrical quantization. To simplify the analysis we will consider only the case of normal incidence of light on the film surface. It allows us to carry out calculations in the approximation known as diagonal response.[4] It asserts that the system responds only at the wave vector of the applied field. More complicated is the case of oblique incidence of light because then the optical characteristics are influenced by the excitations of electron-hole pairs and plasmons and also the inhomogeneous charge density of electron gas.[5-7] In this case the diagonal response approximation is not sufficient, and theory and relations, are much more complicated. Moreover, it does not allow us to observe the direct influence of the geometrical quantization on the optical properties. The theory presented here is simple but it allows us to investigate only this effect and explain some characteristic features of the optical spectra of FEM films.

In order to obtain an expression for the dielectric function of a thin metallic film we use the Ehrenreich-Cohen[8] formula for longitudinal response:

$$\varepsilon(\mathbf{q},\omega)=1-\frac{4\pi e^2}{q^2V}\sum_{\substack{n,n'\\ \mathbf{k}}}\frac{f_0(E_{n,\mathbf{k}})-f_0(E_{n',\mathbf{k}+\mathbf{q}})}{\hbar\omega^{\dagger}-(E_{n',\mathbf{k}+\mathbf{q}}-E_{n,\mathbf{k}})}\,|\langle n',\mathbf{k}+\mathbf{q}|e^{i\mathbf{q}\cdot\mathbf{r}}|n,\mathbf{k}\rangle|^2, \tag{1}$$

where V is the volume of the system, $\omega^{\dagger}=\omega+i\eta$, f_0 is the Fermi-Dirac distribution function, and $E_{n,\mathbf{k}}$ is the eigenenergy of state $|n,\mathbf{k}\rangle$. For the optics we may take the $q\rightarrow 0$ limit and this corresponds to the neglect of the spatial variation of the electromagnetic field across the film. This is a good approximation in the long-wavelength limit for film thickness small in comparison with the light wavelength. It should be stressed that in this wavelength limit the transverse response of the system to the transverse electric field of an incident light wave is equivalent to the longitudinal response of the system to a longitudinal field.[4]

We treat the electrons as a two-dimensional gas in the x and y space directions and the eigenfunctions are in the form of standing waves in the z direction, with the nodes at the limiting surfaces, i.e.,

$$\psi_{n,\mathbf{k}}(\mathbf{r})=(2/dL_xL_y)^{1/2}\exp(ik_xx+ik_yy)\sin[(z\pi/d)n], \tag{2}$$

where $n=1,2,3,\ldots$, and d is the film thickness. From the above relations one can get an expression for the function $\varepsilon(\omega)$ in an explicit form. The result is the same as that obtained in the paper of Wood and Ashcroft,[4] who have applied it to small cubic metallic particles. The identity of the dielectric function of the film and that of cubic particles had been anticipated by Cini and Ascarelli.[9] If the electron relaxation time is introduced in the way proposed by Mermin[10] (see also Ref. 4), then one obtains the real and imaginary parts of the dielectric function in the following form:

$$\mathrm{Re}\,\varepsilon(\omega)=1+S+\left(\frac{4}{\pi}\right)^4\frac{d}{a_0}\sum_{n=1}^{n_F}n^2(n_F^2-n^2)\sum_{\substack{n'=1\\ n'\neq n}}^{\infty}\frac{n'^2[\Delta^2-(x^2+\Gamma^2)][1-(-1)^{n+n'}]}{\Xi}, \tag{3a}$$

$$\mathrm{Im}\,\varepsilon(\omega)=\left(\frac{4}{\pi}\right)^4\frac{d}{a_0}\frac{\Gamma}{x}\sum_{n=1}^{n_F}n^2(n_F^2-n^2)\sum_{\substack{n'=1\\ n'\neq n}}^{\infty}\frac{n'^2[\Delta^2+(x^2+\Gamma^2)][1-(-1)^{n+n'}]}{\Xi}, \tag{3b}$$

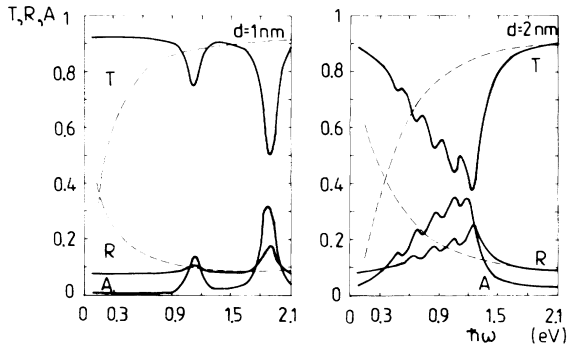

FIG. 1. Computed transmission and reflection spectra of a hypothetical gold film for different thicknesses (assumed parameters in text). Solid line is the prediction of the QSE model; broken line is from the classical Drude model.

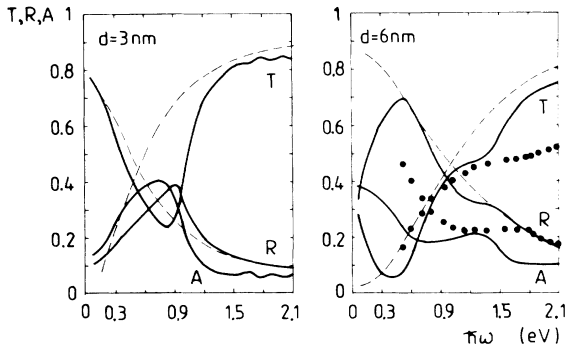

FIG. 2. Computed transmission and reflection spectra of a hypothetical gold film for different thicknesses. Solid line is the prediction of the QSE model; broken line is from the classical Drude model. The points represent the experimental data for Ag film of thickness 6 nm, after Ref. 17.

where

$$\Xi=\Delta^3[(\Delta^2-x^2+\Gamma^2)^2+4x^2\Gamma^2],\quad \Delta=n'^2-n^2,$$

a_0 is the Bohr radius,

$$x=\hbar\omega/(\hbar^2\pi^2/2m^*d^2),\quad \Gamma=(\hbar/\tau)(n_F^2/E_F),$$

$n_F=k_Fd/\pi$ (integer), E_F is the position of the Fermi level of the bulk metal, τ is the relaxation time ($\tau=l/v_F$), l is the mean free path, v_F is the velocity of electrons on the Fermi level, and m^* is the effective mass of the electrons. In Eq. (3a) there has been introduced a parameter S independent of ω which takes into account both the interband transitions and core electrons. The exact value of S for very thin films is not too important, because in this case the dominant role is played by the discreteness of the energy levels of FEM. However, its value is essential in the classical Drude relation for the dielectric function[1] towards which Eq. (3a) and Eq. (3b) tend with increasing film thickness.

We use Eqs. (3a) and (3b) to analyze the optical characteristics of thin metallic films in the near-infrared region; that is, the region where the properties are governed by the free electrons. In the following calculations we use the known relations on transmission T and reflection R[1,2] for a film on a thick substrate. The parameters of the FEM were assumed to be those of gold film (as in our other papers[3,11]): $N=5.9\times10^{22}$ cm^{-3} (concentration of free electrons), $S=7$, $m^*=m_e$ in addition to $l=10$ nm. We have assumed also that the substrate is nonabsorbing and with the refractive index equal to 1.5. Results of calculations are presented in Figs. 1–3. It should be noted that only for very low thickness of the film does the QSE manifest itself in the transmission, reflection, and absorption spectra in the form of well defined peaks. The peaks are much better pronounced on the absorption curves.

According to Eqs. (3a) and (3b) the maxima of absorption appear at the photon energies

$$\hbar\omega=(E_F/n_F^2)(n'^2-n^2),\qquad (4)$$

where $n'+n=1,3,5,\ldots,$.

For larger thicknesses the well defined peaks transform gradually into oscillations but they are visible only in the absorption spectrum. From the above relation it can be seen that their period on the energy scale is hv_F/d. To show this we must put $n'=n_F$ and calculate the energy distance between two following maxima. The oscillatory behavior of the absorption with the same period was predicted within the semiclassical theory.[2,3] So the results of QSE and CSE theory converge for larger film thicknesses. It should be noted that there is a difference in the kind of transitions responsible for the absorption oscillations for very thin (Fig. 1) and those for thicker films (Fig. 3). In the former case the transitions are between the states from below the Fermi sur-

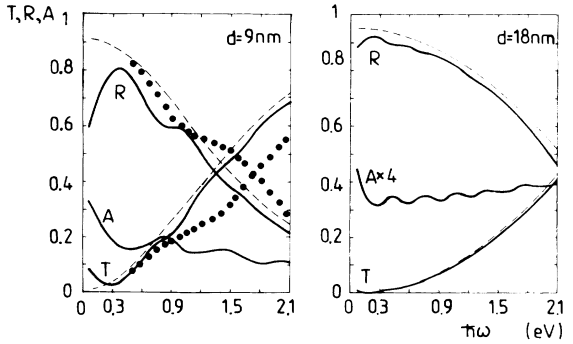

FIG. 3. Computed transmission and reflection spectra of a hypothetical gold film for different thicknesses. Solid line is the prediction of the QSE model; broken line is from the classical Drude model. The points represent the experimental data for Au film of thickness 10.7 nm, after Ref. 18.

face onto it; the transitions to the higher levels should appear in the uv part of the spectrum. In the latter case the transitions from the Fermi surface to the higher empty states take place in the near-infrared part of the spectrum and they are responsible for regular oscillations of absorption.[3] Obviously, in this case also the transitions from the inner levels take place but these have a quasicontinuous spectrum and so they do not lead to the absorption peaks.

For the thickness of about 9 nm (cf. Fig. 3), the oscillations in the spectrum of transmission and reflection diminish in amplitude, retaining some of the characteristic shoulders, at the energy of about 0.9 eV. With increasing thickness, the shapes of the transmission and the reflection spectra approach those predicted by the classical Drude model.[4] Nonetheless, a difference in values still remains. The shift between the curves obtained from the Drude and QSE theories is analogous to that obtained from CSE theory for different values of specularity parameters, namely, between those corresponding to the values $p=q=1$ and those for $p=q=0$. The parameters p and q refer to the lower and the upper film surfaces, respectively. It should be added that also the period of oscillations in the QSE is the same as that in the CSE for p and $q\neq 1$. For $p\neq 1$ and $q=1$ the period is 2 times shorter.[2,3] A similarity of the optical properties obtained from the QSE for the larger film thickness and those from CSE theory for p and $q\neq 1$ may be expected. Namely, in the QSE the surfaces always interact with free electrons, whereas in the CSE the effect of interaction is only when the specularity parameters differ from unity.

In order to observe the QSE in optical properties of thin metallic films we have to possess very thin films of uniform thickness. Unfortunately, films on glass obtained by standard techniques, evaporation or sputtering, are discontinuous of island structure up to a thickness of about 8.0–9.0 nm. However, in the paper of Gillham, Preston, and Williams[12] it was reported that it is possible to obtain gold films of continuous structure even at a thickness of 6 nm, by introduction between the glass substrate and metal of a buffer film of Bi_2O_3. It was found that a 10-nm film of bismuth oxide is sufficient to obliterate all influences of the glass base. The authors stated also that post-deposition heat treatment up to a temperature of 200 °C increases the continuity of films and reduces the surface roughness.

We have applied the recipe of Gillham, Preston, and Williams[12] to obtain thin films of gold. The glass substrates, Corning 7059, were previously covered by a Bi_2O_3 film of thickness 10 nm. On this base gold was deposited by dc sputtering of an Au target (purity 99.99%) in an argon atmosphere at a pressure of about 6 Pa. The deposition rate was a few tenths of a nanometer per second. The film thickness was determined by a quartz monitor. After the deposition, the films were annealed up to 100 °C during four hours. The optical transmission and reflection were measured using a double-beam spectrophotometer (Carl Zeiss). The estimated error was $\Delta T=0.005$ for transmission and $\Delta R=0.03$ for reflection. In Fig. 4 we present the experimental results obtained for films of thickness 4 and 5.8 nm. The resistivity of these films is 78.1 and 23.1 $\Omega/\square$ for 4- and 5.8-nm-thick film, respectively.

In Fig. 4 we have also drawn the theoretical curves calculated from the previously presented theory for thicknesses of 4 and 6 nm and for the values of the remaining parameters the same as in Figs. 1–3. We observe a good qualitative agreement of experiment and theory for 5.8-nm-thick film. A somewhat poorer agreement between the curves is obtained for 4-nm film but the character is similar. The experimental points cannot be described by the classical Drude theory. It is worth noticing that the agreement is not a result of the fitting procedure of the theoretical relations to the experimental points.

We must keep in mind some restrictions regarding the theory and experiment. The applied theory of diagonal response is only an approximation, and one can find many papers on the analysis of optical properties of metals[5–7] and metallic films[13,14] using the wave-vector–dependent dielectric matrix. It was shown there that near the plasma resonance there should appear optical anomalies caused by excitations of excitons and plasmons, but they vanish completely at normal incidence of light.[13] The theory presented here assumes that the films have flat surfaces and are uniformly continuous. The real film is not flat and this must influence the optical characteristics. Some view on this influence may be taken from the analysis of the electrical resistivity of rough films made by Leung.[15] He has shown that for rough films the oscillations resulting from the geo-

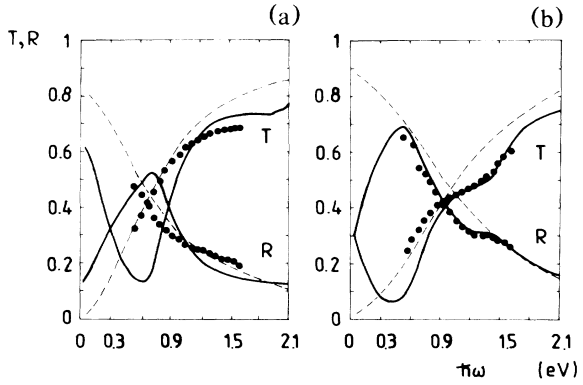

FIG. 4. Experimental transmission and reflection spectra of sputtered Au films of thickness (a) 4 nm and (b) 5.8 nm. The curves were calculated the same way as in Figs. 1 and 2; solid line is from the QSE model and broken line is from the classical Drude model.

metrical quantizations remain. Thus we may expect that also in optical properties the character of the spectra should not be modified though the values of transmission and reflection are changed. At last it seems that the optical characteristic of our films could be influenced by the fact that films though continuous may be formed by electrically connected islands. Many authors have measured and analyzed the optical properties of granular and discontinuous Au films.[16] They have observed the anomalous absorption but in the visible range of spectrum. This absorption was described by the Maxwell-Garnett theory for an array of particles, even though the island particles of these films were irregularly shaped. However, this theory does not produce absorption in the infrared region of spectrum.

Similar shapes of T and R spectra to those presented in Figs. 2 and 3 have been observed by Gasparini and Fraisse[17] for Ag films and by Szczyrbowski[18] for Au films. In Figs. 2 and 3 we have included their experimental data for Ag and Au films, respectively. We are authorized to confront the results for Ag and Au because the free-electron parameters of both materials are close enough.[1,11] We can thus support our statement that the deviation from the classical dependences for thin metallic films is not a result of applied preparation technique or specific material properties.

Finally, we should say that we have not been able to detect experimentally the oscillatory character of the optical properties for very thin films, as expected from the QSE theory. Its absence may be due to the appreciable thickness fluctuations particularly for these films. Nevertheless, we still believe that some of the features of the experimentally observed optical characteristics of films in the range of thickness 4–10 nm have origin in the QSE.

We would like to thank Dr. J. Spałek for valuable discussion and critical reading of the manuscript, and Dr. M. Jachimowski for the technical help.

[1]J. Szczyrbowski, J. Dryzek, and A. Czapla, Thin Solid Films **112**, 175 (1984).

[2]J. Szczyrbowski, K. Schmalzbauer, and H. Hoffmann, Phys. Rev. B **32**, 763 (1985).

[3]J. Dryzek and A. Czapla, Phys. Status Solidi (a) **94**, 665 (1986).

[4]D. M. Wood and N. W. Ashcroft, Phys. Rev. B **25**, 6255 (1982).

[5]K. L. Kliewer, Surf. Sci. **101**, 57 (1980).

[6]T. Maniv and H. Metiu, Phys. Rev. B **22**, 4731 (1980).

[7]R. R. Gerhardts and K. Kempa, Phys. Rev. B **30**, 5704 (1984).

[8]H. Ehrenreich and M. Cohen, Phys. Rev. **115**, 786 (1959).

[9]M. Cini and P. Ascarelli, J. Phys. F **4**, 1998 (1974).

[10]N. D. Mermin, Phys. Rev. B **1**, 2362 (1970).

[11]J. Dryzek and A. Czapla, J. Mater. Sci. Lett. **4**, 154 (1985).

[12]E. J. Gillham, J. S. Preston, and E. Williams, Philos. Mag. **46**, 1051 (1955).

[13]W. E. Jones, K. L. Kliewer, and R. Fuchs, Phys. Rev. **178**, 1201 (1969).

[14]T. Maniv and H. Metiu, J. Chem. Phys. **76**, 696 (1982).

[15]K. M. Leung, Phys. Rev. B **30**, 647 (1984).

[16]C. G. Granqvist and O. Hunderi, Phys. Rev. B **16**, 3513 (1977).

[17]J. P. Gasparini and R. Fraisse, Thin Solid Films **30**, 11 (1975).

[18]J. Szczyrbowski (private communication).