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On the infrared optical response of metallic thin films: a quantum size effect

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Abstract. We present a quantum mechanical calculation of the diamagnetic optical response of metallic ultrathin films. The study shows that in the optical response of ultrathin films (less than 100 Å in thickness), there exists an oscillatory dependence on the film thickness, and the period of the oscillation corresponds to one or a few monolayers. We show that the oscillation can be attributed to the intraband fluctuations of the valence electrons in discrete energy states. For comparison, we present experimental results on the infrared ($\lambda = 9.2 \mu\text{m}$) optical reflectance of Al ultrathin films of thickness 5–112 Å, which exhibit experimentally the predicted oscillations.

1. Introduction

Quantum size effects in the electrical resistivity as well as in the thermodynamic and kinetic characteristics of metallic ultrathin films have been studied in the past few decades [1]. In most cases, the quantum size effects show oscillatory dependencies on the film thickness. Some of the effects might be explained theoretically by considering the scattering of the electrons by randomly distributed impurities [2, 3], or by introducing a microscopic random surface roughness [4–6].

In the present paper, we shall discuss a quantum size effect that was experimentally observed in the infrared optical reflectivity of metallic ultrathin films [7, 8]. In references [7, 8] there was presented a systematic experimental study on the optical reflectance of Al ultrathin films of thickness 5–112 Å deposited on Si and SiO₂ substrates. An important finding of that study was the oscillating behaviour of the reflectance as a function of the film thickness. Thus, oscillations (2.6 Å–3.4 Å in period) can be seen before the film becomes so thick that the reflectance takes the constant bulk value. In the experiments, the light source was at an infrared frequency ($\lambda = 9.2 \mu\text{m}$) which is several orders of magnitude larger than the film thickness. The frequency range is also well away from the possible interband transitions; thus one may expect the diamagnetic effects to play the main role.

It is interesting to note that a local field calculation of the optical diamagnetic response of a metallic quantum well by Keller and Liu [9] resulted in a good agreement with the recently

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observed infrared reflection spectra of Nb films deposited on crystalline quartz of thickness 3–100 Å by Alieva *et al* [10]. However, we have found [7] that the oscillatory dependence in references [7, 8] cannot be demonstrated by using the calculations in references [9]. We then resorted to calculations similar to those in our earlier work on metallic and semiconductor quantum particles, for both diamagnetic [11] and paramagnetic [12] optical properties. We note that in reference [11] numerical results for the diamagnetic polarizability of Au particles show some oscillatory behaviour, which is in detailed agreement with the existing experimental results [13]. We referred to those oscillations as quantum size effects, because of the three-dimensional confinement of the conduction electrons. In more detail, in reference [11] we demonstrated that the oscillating fine structures correspond to an increase of the particle size of such a small microscopic step that only one atom is added in the quantum box (the small particle). In these calculations an assumption of zero temperature was adopted, which means that we considered the electrons to occupy the lowest possible energy states. Hence the last occupied level may be considered as the Fermi level, which differs from the Fermi energy for bulk material. In references [9], the electron-density variation was obtained with the contribution of electrons at various energy levels, and the contribution corresponded to the energy interval between the energy level and the bulk Fermi energy. We believe that the electron density has to be calculated with summation over all electrons regardless of the energy interval, which is why the fine structures were demonstrated only in reference [11].

In the present paper we propose a modified calculation for the situation of one-dimensional confinement. Unlike in reference [11] where an infinite quantum well was adopted, we have used a finite quantum well in our new calculations. What one may expect from this modification is that the wave function associated with an individual electron will extend smoothly outside the edges of the quantum well, or that the possibility of finding the electron inside the quantum well (the metallic thin film) will vary according to the energy level. The situation is, to some extent, similar to that of the semiconductor quantum well considered by Fafard in reference [14]. In such consideration, one would expect a variation in the density of all of the electrons in bound states for different quantum well thicknesses.

With the calculation described above and a simple relation between the electron density and the optical reflectance, we are finally able to demonstrate that there exists an oscillatory dependence of the local electron density on the film thickness even at zero temperature, and the oscillation may be observed in the optical diamagnetic response of metallic ultrathin films. This quantum size effect for the one-dimensional quantum well is distinguishable from the commonly studied quantum size effects in references [1–6], as there is no need to include the microscopic correlations, such as the impurities and surface roughness.

We shall present the theory in section 2. In section 3, we present a comparison of the calculated results to the experimental results from references [7, 8], as well as some discussion.

2. Theory

Let us start with a one-dimensional quantum well description of the metallic thin films as in figure 1. We assume a one-dimensional quantum well with a finite barrier corresponding to the sum of the Fermi energy and work function of the material. For aluminium, $V_0 = 15.95$ eV (see figure 1). The width of the well determines the number of molecular layers in the z -direction. In the case of metals, it is reasonable to assume the zero-temperature limit [11, 12], which means that the conduction electrons stay at energy levels that are as low as possible. The discrete energy levels as well as their corresponding wave functions can be easily calculated.

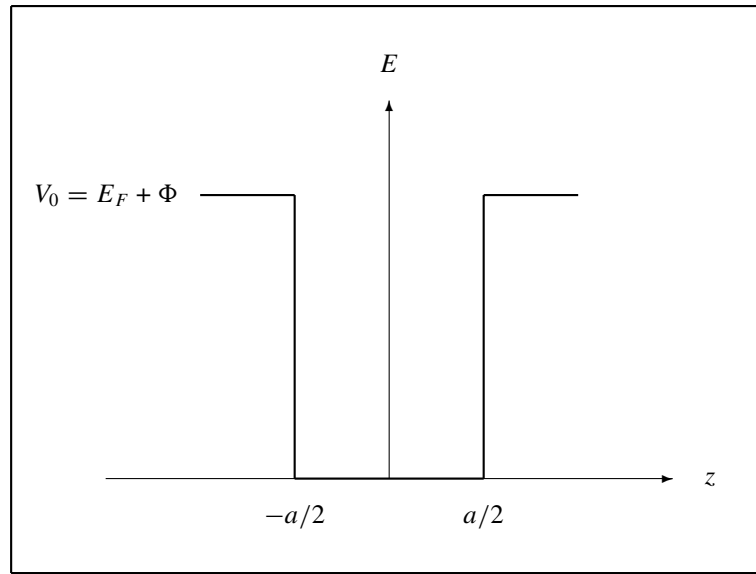


Figure 1. A quantum well with finite depth. The well width is a , and the depth $V_0 = E_F + \Phi = 15.95$ eV for aluminium.

For well width a , the wave functions for bound energy states ($E < V_0$) can be written as

$$\psi(z) = \begin{cases} Ce^{\beta z} & z < -a/2 \\ Ae^{ikz} + Be^{-ikz} & -a/2 < z < a/2 \\ De^{-\beta z} & a/2 < z \end{cases} \quad (1)$$

where

$$\beta = \sqrt{2m(V_0 - E)}/\hbar \quad (2)$$

and

$$k = \sqrt{2mE}/\hbar \quad (3)$$

with m being the electron mass. Using the boundary conditions at $-a/2$ and $a/2$, one can write the coefficients as follows:

$$\frac{A}{C} = e^{(a/2)(-\beta+ik)} \frac{\beta + ik}{2ik} \quad (4)$$

$$\frac{B}{C} = -e^{-(a/2)(\beta+ik)} \frac{\beta - ik}{2ik} \quad (5)$$

and

$$\frac{D}{C} = \frac{k^2 + \beta^2}{2k\beta} \sin(ka). \quad (6)$$

And the coefficient C can be found by using the normalization condition

$$\int_{-\infty}^{+\infty} |\psi(z)|^2 dz = 1. \quad (7)$$

The possible bound states are determined by the following equation:

$$ka = j\pi - 2 \sin^{-1} \left(\frac{\hbar k}{\sqrt{2mV_0}} \right) \quad j = 1, 2, 3, \dots \quad (8)$$

for

$$k = \frac{\sqrt{2mE}}{\hbar} > 0. \quad (9)$$

For an above-determined bound state, if the state is occupied by an electron, the possibility of the electron being found inside the quantum well is

$$n_j = \int_{-a/2}^{+a/2} |\psi(z)|^2 dz. \quad (10)$$

The total number of electrons can be estimated from the number of layers and the number of valence electrons for each atom. These electrons occupy the lowest energy levels. For each level two electrons are allowed because of the spin degeneracy. Therefore, the density of electrons as a function of the film thickness becomes

$$n(a) = \frac{1}{a} \sum_{j=1}^{j=F} 2n_j \quad (11)$$

where the number F corresponds to the uppermost occupied bound state.

The above size dependence in the electron density should influence the macroscopic properties of the films, such as the dielectric function $\epsilon(\omega)$, where ω indicates the angular frequency of light (see reference [11] for a comparison to the three-dimensional cases). For a metal, the dielectric function can be given as

$$\epsilon(\omega) = 1 - \frac{e^2 n_0}{m \epsilon_0 \omega (\omega + i\gamma)} \quad (12)$$

where n_0 is the bulk electron density, $-e$ is the electron charge, ϵ_0 the vacuum permittivity, and γ is a phenomenological damping factor [11]. In the present situation, the electron density fluctuates with the size of the film in the direction across the film. To account for the fluctuation, we Taylor expand the density and consider only the first derivative. Using the bulk plasmon frequency $\omega_p^2 = n_0 e^2 / (m \epsilon_0)$, one finally writes down the dielectric function as a function of the film width as

$$\epsilon(a, \omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \left(1 + \frac{a^2}{N} \frac{dn(a)}{da} \right) \quad (13)$$

where N is the total number of electrons estimated from the layer number and the number of valence electrons for each atom.

It is now straightforward to calculate the reflectance of the film. In order to emphasize the size-dependent optical response of the film alone, and not to get involved with other possible corrections stemming from local field change [9] and substrate reflectance [15], we simply use the Fresnel formula for reflection with vertical incidence, as

$$R(a) = |r(a)|^2 = \left| \frac{\sqrt{\epsilon(a, \omega)} - 1}{\sqrt{\epsilon(a, \omega)} + 1} \right|^2. \quad (14)$$

We present in figure 2 a reflectance curve calculated on the basis of the above formalism with $\gamma = 0.03\omega_p$ and $\lambda = 9.2 \mu\text{m}$. The size of one Al monolayer is chosen to be 2.4 \AA . The reflectance curve in figure 3 shows clearly the expected oscillatory dependence.

3. Comparison with experimental results and discussion

In this section we report our experimental results. The experiments were conducted at room temperature. The samples were Al thin films deposited on Si and SiO₂ (glass) substrates. The

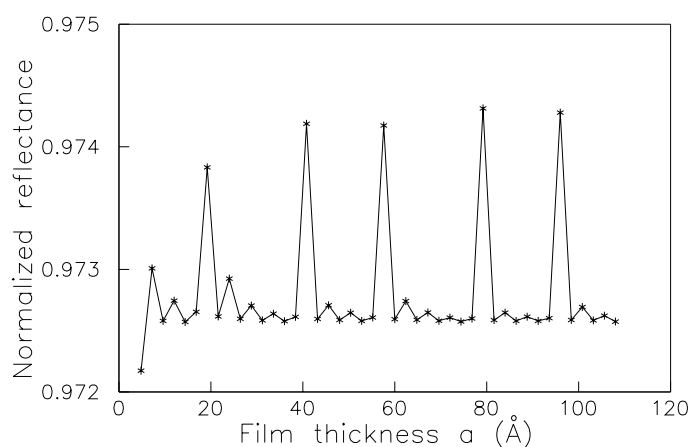


Figure 2. Reflectance as a function of thickness for the Al thin film. Each point corresponds to a new layer. The line is to guide the eyes.

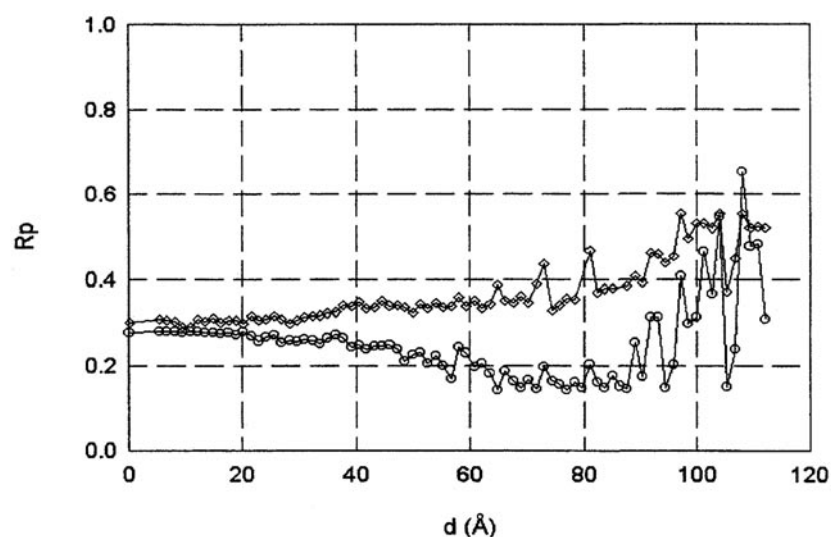


Figure 3. Measured reflectance ($\lambda = 9.2 \mu\text{m}$) as a function of thickness (d) for Al thin films. The substrate was Si (diamonds) or SiO_2 (circles). The lines are to guide the eyes.

thickness of the films ranges from 5 to 112 Å. The samples were prepared with the radio-frequency sputtering technique. The accuracy of the thickness was estimated to be better than 5%.

The light source is a tunable CO_2 waveguide laser which is linearly polarized and tuned to $9.2 \mu\text{m}$ with an output power of 635 mW. The angle of incidence was 7° , and the reflectance was lock-in measured as a function of the film thickness. A detailed description of the experimental set-up and the experiments was published elsewhere [8].

In figure 3 we present two measured curves for the different substrates, where oscillatory fluctuations in the response can be clearly seen. The period of these oscillations was estimated to lie in the range 2.6–3.4 Å. The above experimental results cannot be completely compared

with the calculated curves from the preceding section. Nevertheless, the experimental results support our theoretical finding of a quantum size effect, at least qualitatively.

In passing, we make several comments on our experimental process as follows.

Our samples were prepared with areas of about $1.5 \text{ cm} \times 1.5 \text{ cm}$ on the substrates. On a specific substrate, for each thickness we prepared one film. Hence, the optical reflectance was measured for a group of independent films with different thicknesses. As already mentioned, for each film the accuracy of the thickness was controlled within 5%. For each film we measured the reflectance at 250 different places along a straight line; this was realized by means of a stepping scanner with step $10 \mu\text{m}$. At each step a measurement was done with a light focus spot of $0.5\text{--}1.0 \mu\text{m}$ on the film. Therefore, the measurements were stably repeatable. The accuracy of the measurement was estimated to be 2% (see details in reference [7]).

As a final remark, we point out the fact that in figure 3 the two curves are correlated in such a way that the peaks and valleys in the oscillations appear at the same film thickness values. This is a good indication that the oscillations stem from the properties of the material inside the films, not from the influence of the substrate. On the basis of the calculation in the preceding section, we suggest that the cause of the oscillation is the fluctuations in the electron-density distribution inside the quantum wells.

4. Conclusions

We have demonstrated theoretically and experimentally a quantum size effect in the infrared optical response of a system of metallic ultrathin films. Due to the intraband fluctuation of the conduction electrons in bound energy states, the local electron density changes unevenly as a function of the film thickness. The electron-density fluctuation causes periodic oscillations in the macroscopic optical properties of the quantum well systems. The period of these oscillations is between one and a few monolayers. Finally, we propose that the effects presented can be used as a new technique to characterize metallic ultrathin films in more detail.

Acknowledgment

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References

- [1] See, for instance, Jałochowski M, Hoffman M and Bauer E 1996 *Phys. Rev. Lett.* **76** 4227 for a list of recent references
- [2] Sandomirskii V B 1967 *Sov. Phys.-JETP* **25** 101
- [3] Govindaraj G and Devanathan V 1986 *Phys. Rev. B* **34** 5904
- [4] Leung K M 1984 *Phys. Rev. B* **30** 647
- [5] Trivedi N and Ashcroft N M 1988 *Phys. Rev. B* **38** 12 298
- [6] Fischman G and Calecki D 1989 *Phys. Rev. Lett.* **62** 1302
- [7] Villagómez R 1996 *PhD Thesis* Institute of Physics, Aalborg University, Denmark
- [8] Villagómez R, Keller O and Pudonin F 1997 *Phys. Lett. A* **235** 629
- [9] Keller O and Liu A 1992 *Phys. Lett. A* **167** 301
Liu A and O Keller O 1993 *Phys. Lett. A* **177** 441
- [10] Alieva E V, Firsov E I, Kuzik L A, Yakovlev V A and Pudonin F A 1991 *Phys. Lett. A* **152** 89
- [11] Keller O, Xiao M and Bozhevolnyi S 1993 *Opt. Commun.* **102** 238
- [12] Keller O, Xiao M and Bozhevolnyi S 1995 *Opt. Commun.* **114** 491
- [13] Kreibig U and Genzel L 1985 *Surf. Sci.* **156** 678
- [14] Fafard S 1992 *Phys. Rev. B* **46** 4658
- [15] Villagómez R and Xiao M 1998 *Optik (Stuttgart)* **108** 4