The influence of Fermi surface anisotropy and the charge carrier surface scattering kinetics on the electrical conductivity of a thin metal film in the view of the quantum size effect

I A Kuznetsova, O V Savenko and D N Romanov*

Microelectronics and General Physics Department, P. G. Demidov Yaroslavl State University, 14 Sovetskaya Street, Yaroslavl 150000, Russia

*E-mail: romanov.yar357@mail.ru

Abstract. The electrical conductivity of a thin metal film in an alternating electric field is calculated considering the quantum size effect. The Fermi surface of the metal has the shape of an ellipsoid of rotation, the main axis of which is parallel to the plane of the film. The quantum kinetic equation obtained from the von Neumann equation (the Liouville quantum equation) is solved. The Soffer model is used as the boundary conditions for the distribution function. The dependence of the electrical conductivity on the film thickness is analyzed. A comparison is made with experimental data on the electrical conductivity of bismuth thin films.

1. Introduction

Thin films are widely used as functional, reflective, conductive and dielectric materials in the formation of contacts, the manufacture of printed circuit boards, integrated circuit elements in microelectronics, the creation of light filters, the element base of optoelectronics, in modern lithographic processes. Modern technology makes it possible to produce objects (films, wires, dots) of several nanometers in size, in which electrons exhibit quantum properties. The reduction of the film thickness to the size of the order of the de Broglie wavelength of the charge carriers leads to the quantum size effect due to the quantization of the energy of the charge carriers. The dependence of the electrical conductivity on the thickness of the thin metal film is oscillating, which is shown in [1, 2].

There are several methods for calculating the electrical conductivity of thin metal films, taking into account the quantum size effect. In [3], the effect of surface scattering on the nature of the motion of charge carriers is calculated using the Kubo formalism using the classical kinetic equation. The contribution of impurity scattering is not considered. Surface scattering is described by the surface potential Hamiltonian. The conductivity in the film plane oscillates with a period equal to half the de Broglie wavelength of the electron. However, this method does not establish the possibility of switching from the quantum case to the classical one. This drawback was eliminated in [4] by introducing scattering potentials into the model Hamiltonian, which consider the scattering on the impurities and on both surfaces of the film. Another way to solve the problems was to directly calculate the integral of surface collisions [5]. The relaxation time is calculated considering the total volume and surface scattering and the quantum size effect.
The problem of the electrical conductivity of a thin metal film is solved considering the quantum theory of transport phenomena in this paper. The method of solving the problem is to find the diagonal elements of the density matrix (non-equilibrium distribution function) from the solution of the Liouville equation. The surface scattering of charge carriers is considered through the Soffer boundary conditions [6].

2. Solving method and mathematical calculations

![Diagram of quantum metal film and Fermi surface](image)

**Figure 1.** (a) Quantum metal film in a longitudinal electric field; (b) surface of the Fermi metal film.

We consider a quantum infinite film of metal with thickness $a$, which is located in an external alternating electric field. We introduce a Cartesian coordinate system. The film plane lies in the $XY$ plane (see figure 1 (a)). The origin is located on the lower surface of the film.

The electric field strength vector $\mathbf{E}_{\text{ext}} = (E_x, E_y, 0)$ is located in the film plane and varies according to the harmonic law:

$$\mathbf{E}_{\text{ext}} = \mathbf{E}_0 \exp(-i\omega t),$$

where $\omega$ is the angular frequency of the external field, $\mathbf{E}_0 = (E_{0x}, E_{0y}, 0)$ is the vector of the amplitude of the electric field strength. We assume that $\omega$ is much less than the frequency of the plasma resonance $\omega_p$ in the metal film (in the metal, $\omega_p$ lies in the ultraviolet region $\omega_p \approx 10^{16} \text{ s}^{-1}$).

The thickness of the film is less than the depth of the skin layer (the skin effect is not considered). In this case, the specific electrical conductivity, considering the restriction on the plasma frequency, should be greater than $10^4 \text{ } \Omega^{-1}\text{ m}^{-1}$. Since the electrical conductivity for most metals is in the range of values $10^6 \text{ } \Omega^{-1}\text{ m}^{-1} < \sigma < 10^8 \text{ } \Omega^{-1}\text{ m}^{-1}$, then this condition is met automatically.

The state of charge carriers in a metal is described by the energy, which can be expressed in terms of a quasi-pulse. Let the surface of the constant energy of the metal in the case of a thick film, in which there are no quantum dimensional effects, has the shape of an ellipsoid of rotation, the axis of rotation of which is directed along the axis of the projection of the quasi-pulse of the charge carriers on the $X$ ($p_x$) axis (see figure 1 (b)). As the film thickness decreases, the energy of the charge carriers is quantized and takes a constant value on equidistant ellipses, the centers of which lie on the $p_z$ axis, and the ellipses themselves are located on the ellipsoid of rotation (see figure 1 (b)). The energy of the electrons (holes) takes the form [7]:

$$\varepsilon_n = \frac{p_x^2}{2m_\parallel} + \frac{p_y^2}{2m_\perp} + \varepsilon_{zn}; \quad \varepsilon_{zn} = \frac{p_{zn}^2}{2m_\perp}; \quad n = \pm 1, \pm 2, \pm 3, \ldots, \pm N,$$
where $m_\perp$ and $m_\parallel$ are the transverse and longitudinal effective masses. Since the film thickness is comparable to the de Broglie wavelength of electrons, the projection of the electron momentum $p_z$ takes a discrete series of values, and the projections $p_x$ and $p_y$ take a continuous series of values.

A metal film for free electrons (holes) can be represented as a potential well with infinitely high walls. For a given potential well, the quantization condition of the projection of the quasi-pulse on the $Z$-axis ($p_{zn}$) has the form

$$p_{zn} = \frac{\pi \hbar n}{a}; \; n = \pm 1, \pm 2, \pm 3, \ldots$$

(3)

Since the isoenergetic surface is an ellipsoid of rotation, the specific conductivity of a thin film is a rank 2 tensor. If the main axis of the ellipsoid is parallel to the $p_x$ axis (see figure 1 (b)), then the conductivity tensor is diagonal:

$$\sigma = \begin{pmatrix} \sigma_\parallel & 0 \\ 0 & \sigma_\perp \end{pmatrix}.$$  

(4)

In the case of an arbitrary direction of the main axis of the ellipsoid in the plane $(p_x, p_y)$, the expression for the conductivity tensor can be obtained using the rotation matrix around the axis $p_z$:

$$\sigma_{ij} = M_{ik}^{\mu \nu}(\phi_0)\delta_{kl}M_{lj}^{\mu \nu}(-\phi_0),$$

(5)

where $M_{ik}^{\mu \nu}(\phi_0)$ are the components of the rotation matrix around the $p_z$ axis by the angle $\phi_0$:

$$M_{ik}^{\mu \nu}(\phi_0) = \begin{pmatrix} \cos \phi_0 & -\sin \phi_0 \\ \sin \phi_0 & \cos \phi_0 \end{pmatrix}.$$  

(6)

As a result, from expressions (4-6) we get the following form of the conductivity tensor:

$$\sigma = \begin{pmatrix} \sigma_\parallel \cos^2 \phi_0 + \sigma_\perp \sin^2 \phi_0 & (\sigma_\parallel - \sigma_\perp) \cos \phi_0 \sin \phi_0 \\ (\sigma_\parallel - \sigma_\perp) \cos \phi_0 \sin \phi_0 & \sigma_\parallel \sin^2 \phi_0 + \sigma_\perp \cos^2 \phi_0 \end{pmatrix}.$$  

(7)

The components of the tensor (4) can be found using the kinetic equation. The kinetic equation for charge carriers in a crystal under the action of external fields is derived from the von Neumann equation (the Liouville quantum equation). The Liouville equation describes the evolution of mixed quantum states, which are characterized by a density matrix [8]:

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}],$$

(8)

where $\hat{\rho}$ is the density matrix operator, $\hat{H}$ is the Hamilton operator, $\hbar$ is the Planck constant, and the brackets denote the commutator.

In the framework of perturbation theory, the Hamiltonian of an electron (hole) in a crystal can be represented as

$$\hat{H} = \hat{H}_0 + \hat{U} + \hat{V},$$

(9)

where $\hat{H}_0$ is the Hamiltonian of the free charge carrier in a vacuum, $\hat{U} = -\hat{F}_r$ is the potential energy of the external fields, and $\hat{V}$ is the potential energy of the impurity field in the crystal. Since the external
fields and the field of impurity atoms are small perturbations, it is convenient to work in the basis of the eigenstates $\phi_p$ of the Hamiltonian $\tilde{H}_0$, that is, in the basis of plane waves.

Thus, the Liouville equation (8) in matrix form, taking into account (9), is as follows [8]

$$i\hbar \frac{d\rho_{p'p}}{dt} = (\varepsilon_{n'} - \varepsilon_n)\rho_{p'p} + \sum_{p''} \left[(U + V)\rho_{p'p''} - \rho_{p''p'}(U + V)p''p\right]. \tag{10}$$

The diagonal components of the density matrix $\rho_{pp}$ correspond to the classical distribution function $f_p$ [8]. Let’s write equation (10) for $p' = p$:

$$i\hbar \frac{df_p}{dt} = \sum_{p''} \left[(U + V)p''p - \rho_{pp''}(U + V)p''p\right]. \tag{11}$$

Separately, it is worth noting that the function $f_p$ is a set of distribution functions that describe the state of charge carriers in the plane $(p_x, p_y)$ for each value of $p_z$ (n-th subzone): $f_p = f_n(v_x, v_y)$. The distribution function $f_n$ depends only on the coordinate along the film thickness (the $z$ coordinate), since all points in the $XY$ plane have the same properties: $f_n = f_n(z, v_x, v_y)$. The dependence of $f_n$ on the $z$ coordinate and on the velocity projections $v_x$ and $v_y$ does not contradict the Heisenberg uncertainty principle.

To unambiguously determine the nonequilibrium distribution function $f_n$ from equation (11), it is necessary to set boundary conditions for it. As such, we use the Soffer model [6], which considers the dependence of the specularity coefficients of the lower and upper surfaces $q_{1n}$ and $q_{2n}$ on the roughness parameters $g_1$ and $g_2$ and the angle $\theta$ of the electron incidence on the film surface:

$$
\begin{align*}
(f_n(0, v_x, v_y) &= q_1(g_1, \theta_n)f_{-n}(0, v_x, v_y), \\
(f_{-n}(a, v_x, v_y) &= q_2(g_2, \theta_n)f_n(a, v_x, v_y),
\end{align*}
\tag{12}
$$

$$q_{1,2n}(g, \theta_n) = \exp\left(-\left[4\pi g_{1,2} \cos \theta_n\right]^2\right), \quad g_{1,2} = g_{s1,2}/\lambda_F, \tag{13}$$

where $f_n$ and $f_{-n}$ are nonequilibrium distribution functions of electrons (holes), respectively, with positive and negative velocity projections on the $Z$ axis ($n = 1, 2, 3 ...$); $\theta_n$ is the angle between the charge carrier momentum and the $p_z$ axis; $g_{s1}$ and $g_{s2}$ are the root mean square height of the surface relief for the lower and upper boundaries of the film; $\lambda_F$ is the de Broglie wavelength of an electron with Fermi energy, which depends on the direction in the anisotropic crystal.

The current density $\mathbf{j}$ is defined as follows

$$\mathbf{j} = e \sum_n \iiint \mathbf{v} f_n \frac{2dp_x dp_y}{(2\pi\hbar)^2} \left(\frac{p_{zn} - p_{zn-1}}{2\pi\hbar}\right), \tag{14}$$

and the concentration of charge carriers does not depend on the film thickness and is defined as

$$n_c = \sum_n \iiint f_n \frac{2dp_x dp_y}{(2\pi\hbar)^2} \left(\frac{p_{zn} - p_{zn-1}}{2\pi\hbar}\right). \tag{15}$$

The average values (14) over the film thickness are usually found under experimental conditions.
\[ \langle j \rangle = \frac{1}{a} \int_{0}^{a} j dz, \]  

(16)

Finally, the components of the tensor (4) are obtained from the formal local Ohm's law

\[ \sigma_{\parallel} = \langle j_{x} \rangle / E_x, \quad \sigma_{\perp} = \langle j_{y} \rangle / E_y. \]  

(17)

The kinetic equation (11) is solved in the relaxation time approximation and in the linear approximation with respect to the external electric field. It is assumed that the scattering of charge carriers on impurity ions is much weaker than the scattering on neutral impurity atoms. This approximation allows us to neglect the dependence of the relaxation time on the energy of the conduction electrons [7].

We obtain the following expressions after performing a number of mathematical calculations for the components of the conductivity tensor (4):

\[ \sigma_{\perp \parallel} = \sigma_{0} \Sigma_{\perp \parallel}, \quad \sigma_{0} = \frac{n_{e} e^{2} \tau_{0}}{m_{0}}, \]  

(18)

\[ \Sigma_{\perp \parallel} = \frac{x_{0}}{z_{0,\perp \parallel} x_{\lambda} k_{m,\perp \parallel}} \left( 1 - \frac{3 \rho_{\epsilon}}{64 \chi_{a}^{4} z_{0,\perp \parallel} k_{m,\perp \parallel}^{5/2}} \sum_{n=1}^{N} n \left( 1 - \frac{n^{2}}{\rho_{\epsilon}} \right) \right) \times \left( \frac{2 - q_{1n} - q_{2n} + (q_{1n} + q_{2n} - 2 q_{1n} q_{2n}) \exp(-\Omega_{\perp \parallel n})}{1 - q_{1n} q_{2n} \exp(-2 \Omega_{\perp \parallel n})} \right) \left( 1 - \exp(-\Omega_{\perp \parallel n}) \right), \]  

(19)

\[ \Omega_{\perp \parallel n} = \frac{2 z_{0,\perp \parallel} k_{m,\perp \parallel} x_{0}}{n}, \quad q_{1,2n} = \exp \left( - \left[ \frac{2 \pi g_{s01,2}}{x_{0}} n \right]^{2} \right), \]  

(20)

\[ g_{s01,2} = \frac{g_{s1,2}}{\lambda_{F0}}, \quad z_{0,\perp \parallel} = \frac{\sqrt{\rho_{\epsilon}}}{2 \sqrt{k_{m,\perp \parallel} x_{\lambda} k_{\tau,\perp \parallel}}}, \quad i y_{0}, \quad x_{0} = \frac{a}{\lambda_{F0}}, \quad x_{\lambda} = \frac{\lambda}{\lambda_{F0}}, \quad y_{0} = \frac{a \omega}{v_{0}}, \]  

(21)

\[ \lambda = \bar{v}_{0} \tau_{0} = v_{0} \tau_{0}, \quad \bar{v}_{0} = \frac{2 e F}{m_{0}}, \quad v_{0} = \frac{2 e F_{V}}{m_{0}}, \quad p_{0} = m_{0} v_{0}, \quad \lambda_{F0} = \frac{2 \pi \hbar}{p_{0}}, \]  

(22)

\[ m_{0} = \sqrt{\frac{m_{0}^{2}}{m_{0}}} = \frac{m_{\perp}}{m_{0}}, \quad k_{m,\parallel} = \frac{m_{\parallel}}{m_{0}} = \frac{1}{k_{m,\perp}}, \]  

(23)

\[ \tau_{0} = \frac{3}{t_{\perp}} = \frac{t_{\perp}}{\tau_{0}}, \quad k_{\tau,\parallel} = \frac{\tau_{yy}}{\tau_{0}}, \quad k_{\tau,\perp} = \frac{\tau_{xx}}{\tau_{0}} = \frac{1}{k_{\tau,\perp}}, \]  

(24)

where \( \Sigma_{\parallel} \) and \( \Sigma_{\perp} \) is the dimensionless longitudinal and transverse components of the tensor \( g_{s01} \) and \( g_{s02} \) the roughness parameters for the lower and upper bounds of the film, bezrazmernye on the characteristic wavelength of de Broglie \( \lambda_{F0} \); \( k_{m,\parallel}, k_{m,\perp} \) – dimensionless longitudinal and transverse
effective masses, respectively; \( k_{\|}, k_{\perp} \) – dimensionless longitudinal and transverse relaxation times of charge carriers, respectively; \( x_0 \) – dimensionless film thickness; \( y_0 \) is the dimensionless frequency of the external electric field; \( x_\lambda \) – dimensionless mean free path length; \( \lambda = \bar{v}_0 \bar{\tau}_0 = v_0 \tau_0 \) – characteristic free path length of electrons (holes) without taking into account surface scattering; \( \bar{v}_0 \) and \( \bar{\tau}_0 \) are the characteristic Fermi velocity and free path time of charge carriers in a quantum film; \( v_0 \) and \( \tau_0 \) are the characteristic Fermi velocity and free path time of charge carriers in a macroscopic sample. The free path of electrons (holes) Without taking into account the surface scattering, it does not depend on the film thickness, since this length is a characteristic of the crystal lattice.

3. Result analysis

Figure 2 shows the dependences of the modulus (a) and argument (b) of \( \Sigma_\parallel \) in the quantum case (19-21) (solid lines) and in the quasiclassical case [9] (dotted lines) on the dimensionless film thickness \( x_0 \) at \( k_{m\|} = 1, x_\lambda = 5, y_0 = 0.05, k_{\|\perp} = 2.5 \). Curves 1 – \( g_{s01} = g_{s02} = 0 \); curves 2 – \( g_{s01} = g_{s02} = 0.05 \); curves 3 – \( g_{s01} = g_{s02} = 0.1 \).

Figure 2 shows the dependences of the modulus and argument of the dimensionless longitudinal component of the integral conductivity tensor \( \Sigma_\parallel \) on the dimensionless film thickness \( x_0 \). The solid curves are constructed considering the quantum theory of transport phenomena, and the dotted curves are constructed considering the quasi-classical theory. Considering the quantum size effect and the mirror boundaries, the dependence of the film conductivity on the thickness is oscillating. As the surface roughness increases, the amplitude of the oscillations decreases. The conductivity in the quasiclassical case is greater in modulus and in the argument of the conductivity in the quantum case and in the quasiclassical case, no oscillations are observed. This indicates that the oscillations are caused by quantization of the energy spectrum of charge carriers.

Figure 3 shows the dependences of theoretical and experimental data on the electrical conductivity of a quantum bismuth film [1]. The films were obtained by electron beam evaporation in a Bi target.
vacuum of 99.999% purity at a residual pressure of $\approx 10^{-6}$ Pa. The Fermi surface of electrons in bismuth consists of three symmetrically arranged ellipsoids, the axis of rotation of which is directed parallel to the plane (111). The angle between the axes of rotation is the same and is equal to $2\pi/3$.

The agreement of theoretical calculations and experimental data is observed in the thickness range $a > 70$ nm. Within 10% of the relative error with a film thickness of less than 70 nm, there is agreement between the experimental and theoretical data. As the film thickness decreases, the difference between the theoretical and experimental values increases and becomes significant. The reasons for this difference are electron scattering at the boundaries of crystallites in a polycrystalline bismuth film, inter-valley scattering, changes in the structure of energy zones during the transition to two-dimensional materials (changes in the orientations of ellipsoids), etc.

**Figure 3.** The dependence of the specific conductivity of a quantum bismuth film on the thickness. The dots represent the experimental data [1]. The solid curve is calculated in the quantum case (7, 18-24), and the dotted curve is calculated in the quasi–classical case [9]. The calculation is performed with the following parameters: $\sigma_0 = 2.1 \times 10^4 \Omega^{-1} m^{-1}$, $\lambda = 400$ nm, $\lambda_F = 27$ nm, $k_{m1} = 0.17$, $k_{\perp} = 2.44$, $y_0 = 0$, $g_{s1} = g_{s2} = 1.6$ nm.

### 4. Conclusions

Theoretical model of the electrical conductivity of a thin metal film is constructed, considering the quantum size effect in this paper. The oscillatory dependence of the electrical conductivity on the thickness in the case of the mirror boundaries of the film is shown. As the roughness of the oscillation surfaces increases, they disappear. There is agreement between theory and experiment for the electrical conductivity of Bi thin films, however, in a limited range of film thicknesses.

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