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**Size Effects in Ultrathin Metallic Films**

1. INTRODUCTION

It has long been known that the electrical resistivity of metals is higher in thin films than in the bulk. Common to all previous published works is that the results on the electrical transport properties, derived from the thickness dependent conductivity, are overshadowed by contradictions caused by non-reproducibilities of the experiments.

Advances made in growth techniques now enable control of the structure and thickness of metal films deposited on various substrates in the monolayer range, and measurement of their exotic structures and remarkable properties. The conductivity of thin metallic films is neither a two- nor a three-dimensional problem since the film is always in an intermediate state between the two dimensions.

In 1938 Fuchs [1] published a paper concerning the decrease of the conductivity of the metallic films with decreasing film thickness. This theory was further extended by Sondheimer [2] to include galvanomagnetic effects, and is known as CSE (Classical Size Effect) theory. Size effects were treated classically using the Boltzmann equation for the distribution function of conduction electrons.

In thin film material electrons undergo various scattering mechanisms as volume scattering with mean free path  $l$ , conductivity  $\sigma_{\infty}$  and surface scattering. With decreasing film thickness, diffuse scattering of charge carriers of surface scattering centers contributes more and more to the resistivity. Specular reflection of the electrons at the boundaries does not change the resistivity because the velocity component parallel to the external electric field is unchanged. The scattering parameter  $p$  in the Fuchs-Sondheimer theory describes the part of the conduction electrons that is specularly reflected.

According to Fuchs:

$$\frac{\sigma(d)}{\sigma_{\infty}} = 1 - \frac{3}{2}(1-p)\frac{l}{d} \int_1^{\infty} \left( t^{-3} - t^{-5} \right) \frac{1 - \exp\left(-\frac{d}{l}t\right)}{1 - \exp\left(-\frac{d}{l}t\right) \cdot p} dt \quad (1)$$

where  $\sigma(d)$  is the thickness dependent conductivity.

Two approximations are often used:

for thick film ( $d \gg l$ )

$$\rho_0(d) \approx \rho_{\infty} + \frac{3}{8} \rho_{\infty} \frac{l}{d} (1-p) \quad (2)$$

and for thin film and small  $p$ :

$$\rho_0(d) \approx \rho_{\infty} \frac{4}{3} \frac{1-p}{1+p} \frac{l/d}{\ln(l/d)} \quad (3)$$

$\rho_{\infty}$  is the specific resistivity of bulk material and  $\rho_0(d)$  is the thickness-dependent specific resistivity of thin film. In

this theory the fit of the formulae (2) and (3) to the experimental data allows determine all parameters describing the conductivity in thin films. It is assumed that the film is bounded by two smooth and parallel planes. This assumption is fulfilled only if two-dimensional monolayer-by-monolayer growth mode occurs. Usually the real polycrystalline film is composed of three-dimensional islands with slightly different thickness. Some of the works [3] discussed the surface roughness giving the expressions for the average conductivity. Nowadays, improvement of the technology and the application of new methods for analysis of the surface and thin films allows to produce the metallic films with the thickness of a few monoatomic layers and perfectly smooth surface. This opens the possibilities to study the Quantum Size Effect (QSE) which is expected to occur when the thickness of the film is comparable with the de Broglie wavelength  $\lambda_F$  of the electrons at the Fermi level. In metals  $\lambda_F$  is range of 1Å- about 100 times less than in semiconductors and semimetals.

The theory of QSE in thin films was given by Sandomirski [4]. In the approximation of the potential well the energy  $E$  of the electrons is given by:

$$E = E_{\parallel} + E_{\perp} = \frac{\hbar^2}{2m^*} (k_{\parallel}^2 + k_{\perp}^2) = \frac{\hbar^2}{2m^*} \left( k_{\parallel}^2 + \frac{4\pi^2}{d^2} n^2 \right) \quad (4)$$

where  $n = 1, 2, 3, \dots$ ,  $E_{\parallel}$ ,  $E_{\perp}$  are the energies dependent on the electron motion parallel and perpendicular to the thin film surface. Among many exciting phenomena predicted to occur in ultrathin metallic films, the electrical resistivity oscillations are mostly studied. It follows from the simple theoretical consideration that the period of the resistivity oscillations  $\Delta d$  is determined through relation  $\Delta d = 1/2 \lambda_F$  where  $\lambda_F$  corresponds to the de Broglie wavelength at the Fermi level. This condition can be fulfilled when the thin film thickness is changed continuously but this does not occur during the growth of texturized or monocrystalline layer. One can expected the growth with the minimal increment equal to the monolayers spacing  $d_0$ . Thus the condition  $n 1/2 \lambda_F = d$  can be only at certain circumstances fulfilled.

In work [5] the oscillatory behaviour of the electrical resistivity in double layers of Ag/In and Ag/Ga and in the work [6] in Pt layers as the sign of the QSE is interpreted, but the continuous change of  $d$  is assumed. Recently we succeeded in the preparation of the monocrystalline, ultrathin films of Ag, Au [7] and Pb [8,9,10] with monolayer-by-monolayer growth mode.

This work summarize some of the results obtained during the study of the size effects in electrical resistivity of these metals.

## 2. EXPERIMENT

The Ag, Au and Pb films were prepared in an ultrahigh vacuum (UHV)-system pumped by an ion pump and Ta sublimation pump with a LN<sub>2</sub>-cooled cold wall. The base pressure was  $8 \cdot 10^{-11}$  mbar and the pressure during deposition was kept below  $3 \cdot 10^{-10}$  mbar. The substrates were Si(111) wafers with about  $10 \Omega \text{ cm}$  resistivity at room temperature.

Pb and Ag were evaporated from BN crucibles Au deposition was made from a W basket. The thickness, of the growing films was measured with a quartz-crystal monitor. All resistivity measurements were done at 95 K. During the electrical resistivity measurement the 1017Hz signal from an AC generator was multiplied with the DC signal from the quartz-crystal monitor which is proportional to the mass of the deposited film. The AC-DC product voltage was applied to the Si-substrate with a  $330 \text{ k}\Omega$  resistor in series.

The potential contacts were made from electrochemically etched W wires pressed against the Si crystal. In this manner the film resistance could be measured with high accuracy within a broad dynamic range from 10000 to 10 ohms.

The signal was measured with a lock-in amplifier and was both recorded on a XY recorder and stored in digital form for further evaluation. Other experimental details are given in the works [7,8,9,10].

## 3. RESULTS AND DISCUSSION

The results of the RHEED intensity measurements presented in works [7,10] showed that Ag, Au and Pb grow in a monolayer-by-monolayer fashion. In order to bring out the details of the experimental curve of the resistivity ( $\rho$ ), the Sondheimer approximation (2) was fitted to the data. A typical result for Pb thin film is shown in Fig. 1.

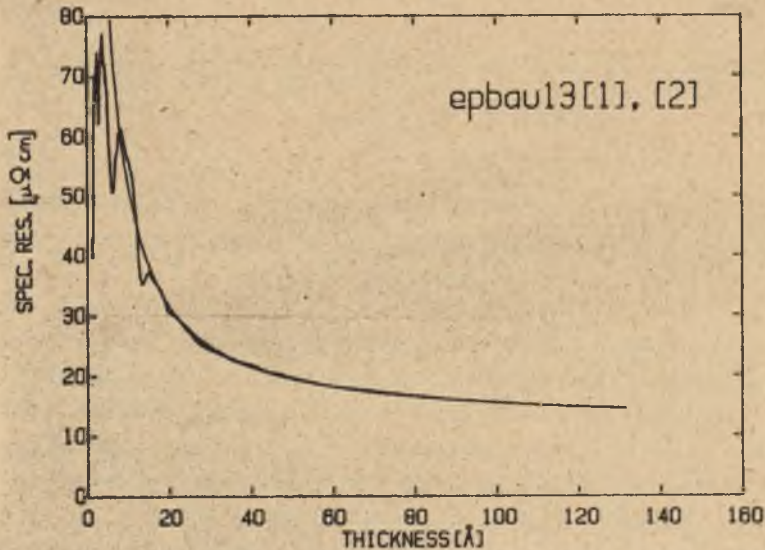


Fig. 1. Measured and fitted  $\rho(d)$  dependence of the Pb ultra-thin film deposited on Si(111)/(6x6)Au at 95K. The smooth curve is drawn according to the formula (2) with  $\rho_{\infty} = 1.14 \cdot 10^{-5} \Omega \text{ cm}$  and  $l(1-p) = 95 \text{ \AA}$ .

Within the thickness range from about 30  $\text{\AA}$  up to 130  $\text{\AA}$  the fit is very good. Deviations from the dependence described by the formula (2) are caused by the CSE and QSE. The difference  $\rho - \rho_0$  shows the fine structure of the  $\rho(d)$  dependence as is shown in Fig. 2. For the Pb deposited on Si(111)/(6x6)Au substrates the resistivity minima every 2 monolayers (ML) is seen.

The Fermi energy of bulk Pb is  $E_F = 9.8 \text{ eV}$  and its effective mass in [111] direction  $m^* = 1.14 m_0$  [1] so that  $\lambda_F = \hbar / (2m^* E_F)^{1/2} = 3.66 \text{ \AA}$ . The (111) monolayer thickness in the bulk is

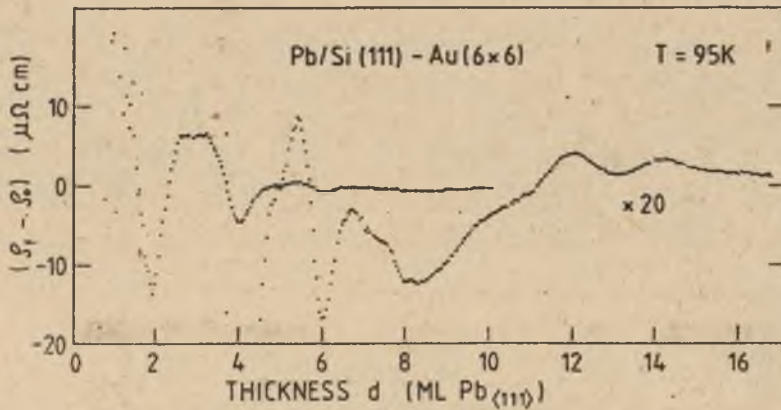


Fig. 2.  $\rho_F - \rho_0$  difference for Pb ultrathin film. Note the resistivity minima with separation of 2 ML.

$d_0 = a/\sqrt{3} = 2.86 \text{ \AA}$ . Thus we have  $(\lambda_F/2)$ :  $d_0 = 1.83:2.86 = 2:3.12 \approx 2:3$  and as a consequence the QSE condition is only approximately fulfilled for 2, 4, 7, 9 and 20 ML of Pb. Changing the growth conditions it was possible to suppress the QSE and to enhance the CSE. This is discussed in the paper [8] where the resistivity oscillations with 1 ML period are presented. A weak 1 ML resistivity oscillations are seen also in fig. 2. Those oscillations are caused by the periodic change of the surface roughness. During the monolayer-by-monolayer growth the smooth surface (and high p-value in formula (2)) is obtained when the top layer is completely filled.

Otherwise, for partially filled upmost monolayer the p-parameter is small. Thus CSE oscillations in resistivity reflect the monolayer-by-monolayer growth of metallic films.

An illustrative example is the Au thin film. In Au, in the 111 direction (growth direction) there is energy gap near Fermi energy and for the sample with (111) planes parallel to the substrate no QSE in electrical resistivity are expected. The similar situation is for Ag but the growth mechanism does not allow to observe also CSE [7].

In Fig. 3 we present the experimental data for Au on Si(111)/(7x7) substrate at 95 K. The plot  $(\rho_F - \rho_0)/\rho_0$  is made

with fitting parameters  $l(1-p) = 352 \text{ \AA}$  and  $\rho_{\infty} = 4.03 \cdot 10^{-6} \Omega \text{ cm}$ .

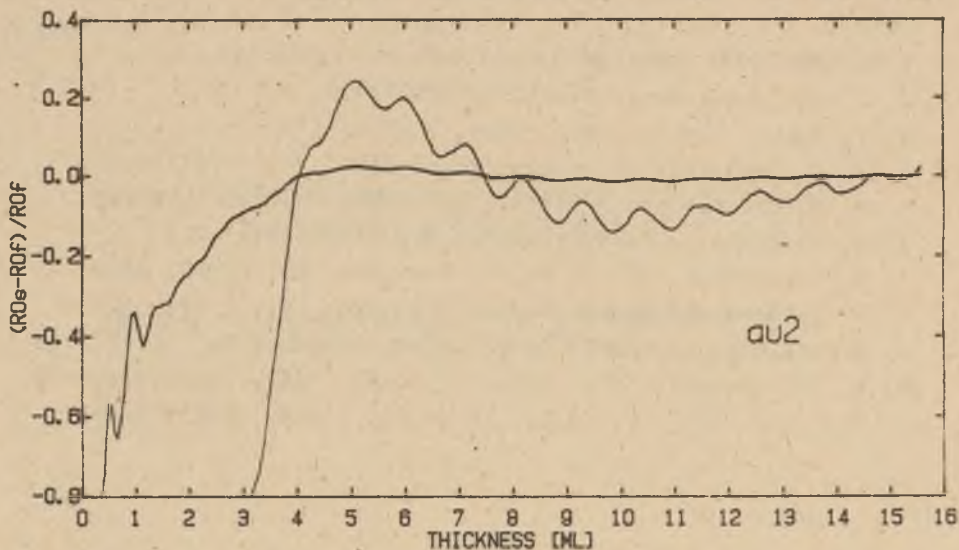


Fig. 3. Normalized specific resistivity  $(\rho_f - \rho_0) / \rho_0$  thickness dependence for Au ultrathin film deposited on Si(111)/(7x7) at 95 K.

In this case a pure CSE resistivity oscillations are seen. A shift of the resistivity minima vs. integer number of ML is caused by the different growth mode in initial stage of deposition.

In conclusions, both CSE and QSE resistivity oscillations have been seen in electrical resistivity measurements. Both phenomena require monolayer-by-monolayer growth mode.

The QSE can be observed only in the case where an integer number of the  $\lambda_F/2$  is equal an integer number of  $d_0$  and if the Fermi energy level is crossing energy band in direction perpendicular to the thin film substrate.

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