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Thickness Dependence of Resistivity Anisotropy of Gold Thin Films

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Abstract

The movement of electrons in metals is still a highly investigated topic today due to its relevance to modern electronics. As nanotechnology becomes a larger part of our lives, a clear understanding of the behavior of nanomaterials is sought after. As the thickness of metallic films drops below its mean free path, its resistivity deviates from the Free Electron Model's predictions. This paper examines resistivity's relationship to mean free path and electrical anisotropy that results from grain boundaries and external surfaces at thicknesses below mean free path in gold thin films. Electrical characterization was performed on various film thicknesses, and the extent of anisotropy is discussed.

Introduction

Thin film science can be described as anything to do with thin material coatings or layers that range from several micrometers to a few nanometers. Not only are they a popular research topic at universities around the world, but their applications are practically limitless. Most electronics we possess today have thin coatings within them to alter their electronic properties, especially in conjunction with semiconductors. Detectors, catalysts, filters, and optics all utilize thin films to some extent. An understanding of the properties of thin films is crucial to the advancement of technology.

Gold is an ideal material for use in electronics. Gold has excellent optical reflectivity (>96%) for infrared light, which is still a highly valued property today. In addition, gold has excellent resistance to corrosion, tarnishing, and is less reactive, unlike more common metals such as silver, copper, and aluminum. High electrical and thermal conductivity make gold a perfect electrical contact or protective material (Corti, 2004). In practice, dozens, or hundreds of small electrical contacts or even wires made of gold will be used within an electronic device. During lithography, the process of etching circuitry and channels onto semiconductor chips, gold is invaluable as an effectively inert electrical contact.

An understanding of electrical conductivity is required before anisotropy can be discussed. Conduction in metals is due to how freely electrons may move, which is significant in conductors, moderate in semiconductors, and negligible in insulators. The electrons within a solid are arranged in what are called energy bands (Kittel, 1996). They are essentially regions or "levels" of energy an electron may possess, and the spaces between these bands are called band gaps. Gold has no band gap, which is why it is an excellent conductor. The energy bands of gold are stacked continuously upon one another. Therefore, electrons in the valence band of gold, which are electrons "attached" to atoms in their outer most orbitals, can freely move into the conduction band, which is where they contribute to electrical current.

Conductivity σ_0 is an intrinsic property of a solid dependent on the movement, density, and energy of electrons within. One of the most convenient yet accurate representations of conductivity is the Sommerfeld Free Electron Model given here.

$$\boldsymbol{j} = \sigma_0 \boldsymbol{E} \qquad (1)$$

$$\sigma_0 = \frac{ne^2\tau}{m} \qquad (2)$$

Where n is the number of electrons per unit volume, m is the mass of an electron, τ is the collision time, and $e = -q$. Electrical resistivity is then defined as the reciprocal of σ_0, where $\rho_0 = 1/\sigma_0$. So greater resistivity equates to lower conductivity and vice versa. Observe that σ_0 is only dependent on n and τ, and n is a constant dependent only on the material, unless the material has been doped with another element. Collision time τ is then of great interest, which is defined as follows (Kittel, 1996).

$$\tau = \frac{\lambda}{v_F} \qquad (3)$$

$$v_F = \frac{\hbar}{m}(3n\pi^2)^{1/3} \quad (4)$$

v_F is the Fermi velocity, which is the velocity of electrons over the Fermi surface, and λ is the mean free path of electrons. Physically, the mean free path λ is how far electrons travel in a material before they collide with an obstacle. The term "obstacle" is quite vague because it may refer to anything from phonons, grain boundaries, or even other electrons. We may now revise our definition of conductivity to yield the following:

$$\sigma_0 = \frac{ne^2\lambda}{mv_F} = \left(\frac{e^2n^{2/3}}{3^{1/3}\pi^{2/3}\hbar}\right)\lambda \qquad (5)$$

Conductivity is therefore directly proportional to the mean free path of electrons for a pure undoped metal, and resistivity is inversely proportional to the mean free path λ. In bulk gold, or when the thickness t is much greater than the mean free path, resistivity is a near constant. However, when the thickness of a film is smaller than its mean free path or $t < \lambda$, then the Sommerfeld Model begins to break down. At thicknesses below the mean free path, the motion of electrons is dominated by grain boundaries and the external surfaces, as well as by crystal lattice defects and impurities (Gall, 2016; Gilani, 2018). A grain boundary is where two misaligned grains meet in a solid and do not merge properly and may range from being a micrometer to a millimeter in size. Due to the increasing importance of nanotechnology, it is important to develop an understanding of how resistivity changes as thin films become thinner.

It's been shown that the electrical resistivity of gold thin films increases dramatically as the thickness of the film drops below 38 nm (Gall, 2016; Fuchs, 1938). This distance coincides with the mean free path of electrons within gold at room temperature. For reference, the mean free path of bulk gold, or the average distance an electron will travel before collision, is 37.7 nm (Gall, 2016). Resistivity's dependence on thickness becomes more complicated when anisotropy is considered. Anisotropy refers to a directional dependence, and electrical anisotropy is a directional dependence for a material's conductivity. For example, if a thin film was measured to have higher resistivity along its length than its width, then it would be referred to as anisotropic. Correcting Sommerfeld's Free Electron Model is possible but is rigorous and tedious (Sondheimer, 1952; Englman, 1956). Instead, an experimental approach can be taken to observe and quantify electrical anisotropy.

In his 1970 paper, "Method for Measuring Electrical Resistivity of Anisotropic Materials," Montgomery outlines a method for measuring anisotropy in conductors. Anisotropic conductors are described values for resistivity ρ_i are required. These values are calculated via the following formulas:

$$(\rho_1\rho_2)^{1/2} = Hl'_3R_1 \quad (6)$$

$$(\rho_2/\rho_1)^{1/2} = (l_2/l_1) \times (l_1'/l_2') \qquad (9)$$

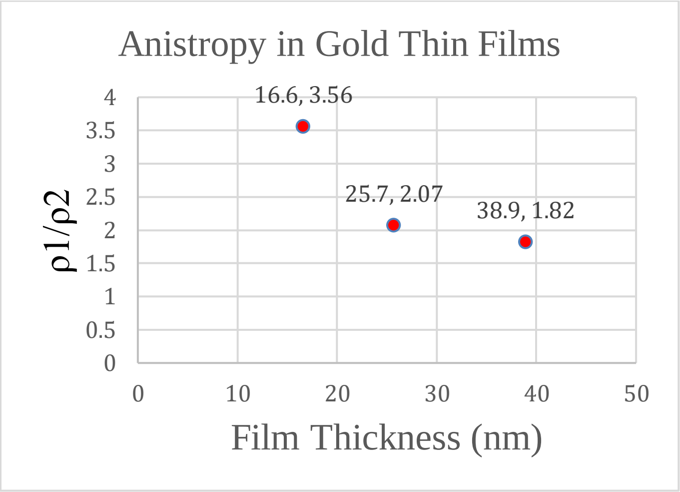
Where H is proportional to sample dimensions l_1'/l_2' and R_1 is the ratio of voltage to current for that dimension These equations allow us to calculate a ratio that describes the anisotropy of a sample, in addition to resistivities for each direction.

Methods

Gold was evaporated with a Cooke Vacuum Products evaporation chamber, vacuum pump, and power supply. 99.99% purity gold was placed on a titanium boat secured between two electrodes inside the chamber. Microscope slides were fastened to the roof of the chamber to act as a substrate. Evaporation was carried out slowly at 220 amps and between chamber pressures at 10^{-6} torr. Samples were stored inside a desiccator to prevent oxidation until ready for testing.

Electrical characterization was performed with an Elenco Precision power supply model XP-660. The samples were cut down to a smaller rectangular size to ensure easy measurements. A conductive silver paint (silver in iso-butyl methyl ketone) was used to attach copper wires at the four corners of the samples as uniformly as possible. As described in the Montgomery method for determining anisotropy, current and voltage measurements were taken across the width of the sample, then the connections were rotated 90° to take current and voltage measurements across the length. Applied voltages up to 20 volts were utilized and varying resistors in the 100 kilo-ohm range were used in the circuit to keep the current below 10 milliamps. I-V curves were then plotted to obtain values for R_i.

Results and Discussions



Graph 1: Ratio of ρ_1/ρ_2 versus gold film thickness

	Sample 1	Sample 2	Sample 3
Thickness (nm)	16.6	25.7	38.9
ρ_1/ρ_2	3.56	2.07	1.82
ρ_1 $(\Omega \cdot m)$	8.43E-07	3.24E-07	5.42E-08
ρ_2 $(\Omega \cdot m)$	2.37E-07	1.57E-07	2.98E-08
$\sqrt{\rho_1\rho_2}$ $(\Omega \cdot m)$	4.47E-07	2.26E-07	4.02E-08

Table 1: Values of resistivity anisotropy ratio ρ_1/ρ_2, and individual resistivities ρ_1 and ρ_2

The three samples fabricated showed varied amounts of anisotropy. The greater the ratio ρ_1/ρ_2, the greater the degree of anisotropy. The 16.6 nm sample has the greatest ratio of 3.56, indicating the resistivity across l'_1 is 3.56 times greater than across l'_2. This is to be expected as a thinner sample should be less uniform and exhibit significant anisotropy below the mean free path of gold.

Sample 2 still displays anisotropy, being roughly twice as resistant to conduction. Sample 3 is interesting because its anisotropy ratio is 1.82 which is only a small decrease from sample 2, yet its resistivity is far lower than sample 2. In fact, the resistivity of sample 3 is near that of bulk gold, known to be $2.44 \cdot 10^{-8}\ \Omega \cdot m$, while being just a little over a dozen nanometers thicker than the previous sample whose resistivity was far greater than the bulk value. This is because the thickness of sample 3, 38.9 nm, is slightly greater than the mean free path its electrons, 37.7 nm. Although just barely thicker, most electrons in sample 3 are now travelling a distance expected of electrons in gold. Unlike samples 1 and 2, the mean free path is no longer restricted by the external surfaces. However, at 38.9 nm, the sample is still only a several dozen atomic layers thick, meaning its internal crystal arrangement is still largely random. This randomness will still produce significant anisotropy.

Graph 1 displays the trend of anisotropy versus film thickness. The plot is a negative exponential, which was expected. As thickness decreases, the ratio ρ_1/ρ_2 should approach infinity, and as thickness increases, this ratio and the points should trend towards one. The uniform cubic structure typical of gold becomes more prevalent as thousands and millions of atomic layers are stacked, leading to the isotropic behavior we expect of bulk gold.

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