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Resistivity of thiol-modified gold thin films

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ABSTRACT

In this work, we study the effect of thiol self assembled monolayers on the electrical resistivity of metallic thin films. The analysis is based on the Fuchs–Sondheimer–Lucas theory and on electrical transport measurements. We determined resistivity change due to dodecanethiol adsorption on gold thin films. For this purpose, we controlled the deposition and annealing temperatures of the films to change the surface topography and to diminish the effect of electron grain boundary scattering. Results show that the electrical response to the absorption of thiols strongly depends on the initial topography of the surface.

1. Introduction

Self-assembled monolayers (SAMs) have been proven useful in different fields: biology, chemistry, material science and physics, among others. The interest in these systems is mainly due to the possibility of forming ordered molecular overlayers, over the surface of metallic substrates to be used as protective coatings, lubricants an even molecular electronics. One of the simplest ways to get a SAM is through thiol adsorption [1]. This process is performed by immersing the metal substrate into a thiol solution for a few hours. The simplicity of this method has transformed thiols in one of the most studied compounds to form SAMs. In addition, thiols' functional groups can be modified by different functionalization alternatives, opening technological applications and basic research problems [2]. For example, dithiols have been used as models to study the conductance through organic molecules [3,4]. Electrical response has also been examined in systems that use thiols as coating of Ag-nanoparticles [5] and as linkage between Au-nanoparticles [6,7]. The use of thiols as protective layers of copper films results in a reduction of the amount of surface oxide formed under the exposure to atmospheric environment [8,9]. Both in research and applications, an important subject is the formation of SAMs, in this sense the preferred system to study this growth process is: thiol adsorption on gold substrates [10,11].

When thiols are used as coating for metals, a relevant issue is the effect of the deposited molecules on the metal electrical response. To study this response, often, a thin film is used as metallic substrate and adsorption is performed by the immersion in a thiol solution at room temperature [1]. In these conditions, the above question can be addressed in a more simple way: how does the presence of thiols affect the resistivity of the thin metallic film at room temperature.

The resistivity of thin metallic films is determined mainly by a series of different scattering mechanisms, which contribute to its magnitude. At room temperature, these mechanisms are: electron-phonons scattering, electron-grain boundary scattering and electron-surface scattering. One way to verify the influence of each one separately is to try to isolate or reduce the effect of the others, for example by changing the surface morphology or grain sizes in a thin film [11–14]. Since thiols will mainly affect the electron-surface scattering process [11], we need to diminish the electron-grain boundary scattering (electron–phonon scattering is already determined by the temperature). Then, we can address the questions through a size effect electrical transport model.

The standard size effect model is known as Fuchs–Sondheimer theory [15,16]. This model introduces the effect of electron surface scattering through a specularity parameter, which represents the fraction of charge carriers performing “specular collisions” with the film surface. That is, the parallel momentum component to the surface of the electrons is conserved, and the normal component is reversed, after collision. Other charge carriers perform “diffuse collisions”, modifying its momentum and generating resistivity.

From an experimental point of view, to decrease the effect of electron grain boundary scattering, we need to increase the mean grain diameter and improve the interface between grains. This can be achieved controlling the deposition and annealing temperature of the film [12–14]. In addition, this thermal process can be used to modify the surface topography, controlling the dimension and roughness of the surface terraces [17,18].

This report describes the effect of thiol monolayers on the electrical resistivity of metallic thin films. For this purpose a standard model for the electrical conduction of thin films has been used. It is based on

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Fuchs–Sondheimer–Lucas theory [15,16,19] and on the Namba model [20]. Transport measurements have been performed in the system dodecanethiol-gold (C_{12}/Au). Thiols were self-assembled on gold thin films, with fabrication conditions optimized to verify electron surface scattering effects in different surface topographies.

2. Theory

Most thiols are bound to Au with their S head group adsorbed on the metallic surface, therefore, a new scattering center is created by each molecule, inducing an increase in the resistivity of the film [11,21,22]. This phenomenon can be modeled as a change in the electron surface scattering due to the thiol adsorption. The first theory describing the effect of the electron surface scattering on the electrical conductivity of a metallic thin film was published by K. Fuchs [15] in 1938. In 1950, E.H. Sondheimer [16] generalized this theory for galvanomagnetic effects.

The Fuchs–Sondheimer theory (FS) [15,16], as it is currently known, describes the electrical conduction process through a Boltzmann Transport Equation. The effect of electron-surface scattering on the resistivity is introduced through a specularity coefficient "P". This coefficient is imposed on the electron distribution function as a boundary condition at the metallic film surface. If a fraction of the charge carriers exhibit a (1-P) different from zero, it means they are inelastically scattered, which induces an increase of the resistivity. This theory was generalized by Lucas [19], allowing two different specularity parameters P and Q, associated to the upper (free surface) and lower (metal-substrate) interface, respectively. The resistivity predicted by this Fuchs–Sondheimer–Lucas (FSL) theory, can be calculated from [19]:

$$\frac{\rho}{\rho_{0\,FSL}}(\kappa,P,Q)=\frac{\varphi_{P,Q}(\kappa)}{\kappa} \tag{1}$$

with

$$\frac{1}{\varphi_{P,Q}(\kappa)}=\frac{1}{\kappa}-\frac{3}{4\kappa^2}\int_1^{\infty}\left(\frac{1}{x^3}-\frac{1}{x^5}\right)\times\frac{(1-\exp(-\kappa x))[2-P-Q+(P+Q-2PQ)\exp(-\kappa x)]}{1-PQexp(-2\kappa x)}dx$$

and $\kappa = t/\ell_0$; where t represents the film thickness and ℓ_0 the bulk mean free path (in the absence of surface scattering).

When the film is very thin, variations of the thickness along the film can produce a sizable resistivity change, which is higher in magnitude than the FSL prediction [20]. This geometric effect can be added through the Namba model [20]. In this model, the resistivity change can be introduced by considering a one dimensional sinusoidal film thickness distribution $t(x)$:

$$t(x)=\bar{t}+t'sin(kx) \tag{2}$$

where $\bar{t}$ is the mean thickness, t' is the amplitude of the thickness oscillation, and k describes the spatial periodicity of the oscillation. Considering these two models the resistivity increase can be computed from Eqs. (1) and (2) as:

$$\frac{\rho}{\rho_0}(\bar{t},t',\ell_0,P,Q)=\frac{\bar{t}}{L}\int_0^L\frac{\frac{\rho}{\rho_{0\,FSL}}\left(\frac{t(x)}{\ell_0},P,Q\right)}{t(x)}dx \tag{3}$$

with L, being the length of the sample. This expression should reproduce fairly well the electrical conduction process, when the electron-grain boundary scattering is negligible.

In this theory, a change in the electron surface scattering appears as a modification of the specularity parameter. When the film resistivity increases, due to thiol adsorption, this effect can be modeled by considering a reduction of the specularity parameter associated to the upper surface. Thereby, the effect of the thiols on the resistivity can be calculated from:

$$\frac{\Delta\rho}{\rho}=\frac{\rho_{\text{with thiols}}-\rho_{\text{without thiols}}}{\rho_{\text{without thiols}}}=\frac{\frac{\rho}{\rho_0}(\bar{t},t',\ell_0,P_T,Q)-\frac{\rho}{\rho_0}(\bar{t},t',\ell_0,P_C,Q)}{\frac{\rho}{\rho_0}(\bar{t},t',\ell_0,P_C,Q)} \tag{4}$$

where P_C represents the specularity parameter of the gold surface without thiols (clean), and P_T represents the specularity parameter of the metal surface completely covered by thiols.

In order to explore the resistivity increase within this model, Eq. (4) has been used to calculate the changes induced by a dodecanethiol SAM on a gold thin film at room temperature. In this system the bulk mean free path, ℓ_0, is ~38 nm and the bulk resistivity, ρ_0, is ~22×10^{-9} Ω m [23].

The dependence of the resistivity increase on the specularity parameters was evaluated for the clean film (P_C) and the thiols covered surface (P_T). For this calculation the gold film thickness, $\bar{t}$, was fixed at 50 nm and a $t' = 2$ nm was included. The specularity parameter of the lower interface was fixed at $Q = 0.2$ [13]. The result of this evaluation is presented in Fig. 1a, as a resistivity increase vs the variation of the specularity parameter ($\Delta\rho/\rho$ vs $|\Delta P|$). The different curves depicted in this figure, correspond to different specularity parameters for the clean film (P_C). First, we note that the upper limit for the resistivity increase is 16%, this happens when the specularity parameter changes from 1 to 0 (completely specular surface to completely diffuse scattering). Previous reports for similar systems indicate a resistivity increase, $\Delta\rho/\rho$, between 2% and 7%. For example, for C_{16} on a 50 nm thick Au-film, the resistivity increase is between 2% and 4% [11,21], while for C_{10} on a 25 nm thick Au-film, the resistivity increase was 7% [24].

If P_C is lower than 1, the resistivity increase is automatically limited to the highest allowed specularity parameter variation (see Fig. 1a). Also, there is an almost linear dependence of $\Delta\rho/\rho$, under small variations in $|\Delta P|$. Therefore, as shown in Fig. 1, the change in resistivity is mainly given by the specularity parameter difference, $|\Delta P|$, independently of the initial specularity parameter of the clean film, P_C.

This model can also display the resistivity increase as a function of the gold film thickness. Fig. 1b shows this dependence, $\Delta\rho/\rho$ vs $\bar{t}$, for three different variations of the specularity parameter, $|\Delta P|$. The increase in resistivity due to a decrease in the thickness of the film is expected in a theory including size effects. In other words, the

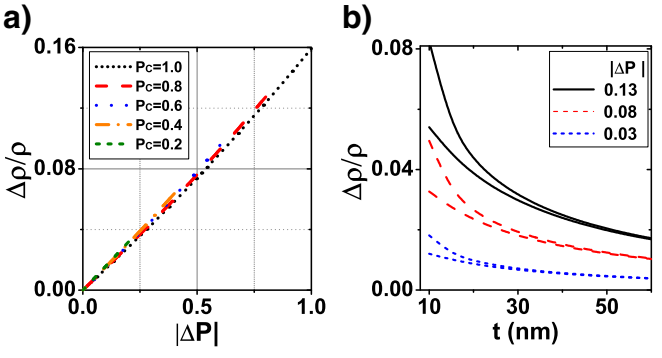

Fig. 1. a) Prediction for the resistivity increase $\Delta\rho/\rho$ due to the specularity parameter variation $|\Delta P|$, for a 50 nm thick gold film at room temperature. Each curve was calculated for a different initial specularity parameter of the clean film, P_C, as indicated in the legend. b) Resistivity increase $\Delta\rho/\rho$ as a function of the mean film thickness: $\bar{t}$. All curves were calculated for $Q = 0.2$, and different values for $|\Delta P|$, as indicated in the legend. For each $|\Delta P|$ we considered in addition different values for t': 9 and 1 nm, which correspond to the upper and lower curves, respectively.