Measurement and interpretation of the mid-infrared properties of single crystal and polycrystalline gold

D. Canchal-Arias [1], P. Dawson *

School of Maths and Physics, Queen's University, Belfast BT7 1NN, United Kingdom

Abstract

The contribution of electron–phonon scattering and grain boundary scattering to the mid-IR ($\lambda = 3.392\ \mu m$) properties of Au has been assessed by examining both bulk, single crystal samples—Au(111) and Au(110)—and thin film, polycrystalline Au samples at 300 K and 100 K by means of surface plasmon polariton excitation. The investigation constitutes a stringent test for the in-vacuo Otto-configuration prism coupler used to perform the measurements, illustrating its strengths and limitations. Analysis of the optical response is guided by a physically based interpretation of the Drude model. Relative to the reference case of single crystal Au at 100 K ($\varepsilon = -568 + i\,17.5$), raising the temperature to 300 K causes increased electron–phonon scattering that accounts for a reduction of $\sim$40 nm in the electron mean free path. Comparison of a polycrystalline sample to the reference case determines a mean free path due to grain boundary scattering of $\sim$17 nm, corresponding to about half the mean grain size as determined from atomic force microscopy and indicating a high reflectance coefficient for the Au grain boundaries. An analysis combining consideration of grain boundary scattering and the inclusion of a small percentage of voids in the polycrystalline film by means of an effective medium model indicates a value for the grain boundary reflection coefficient in the range 0.55–0.71.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Surface waves—Plasmons; Reflection spectroscopy; Atomic force microscopy; Electrical transport (conductivity, resistivity, mobility, etc.); Gold; Polycrystalline thin films; Grain boundaries; Single crystal surfaces

1. Introduction

The issues of interface and grain boundary scattering of electrons in metals is of fundamental importance across a very broad frequency band, ranging from d.c. electrical measurements to optical frequency response. Much of the current

---

* Corresponding author. Tel.: +44 2890 973532; fax: +44 2890 973110.
  E-mail address: p.dawson@qub.ac.uk (P. Dawson).
[1] Current address: Intel, Collinstown Industrial Park, Leixlip, County Kildare, Ireland.

interest is driven by nanoscaling considerations. In the case of electrical properties the interest is driven by reduction in the width of thin-film electrical interconnects to significantly below the 100 nm level [1] and by issues such as the formation of nanocontacts [2]. In the optical regime, metallic entities on the scale of ∼100 nm or less exhibit remarkable resonance properties due to the excitation of localised plasmon modes; these range from the well-known Mie modes of a metallic sphere [3] to, for example, the modes supported on metallic nanorods [4] and the novel surface plasmon modes on reduced geometry structures such as those explored by Kottmann et al. [5].

The background to such investigations is the measurement and understanding of samples in bulk and thin film form. However, the extension from thin film samples to those for which all three dimensions are on the nanoscale is not a matter of simple iteration since new physical phenomena come into play. Nonetheless, examination of single-crystal, bulk material defines the basic material resistivity, ρ, and the optical frequency dielectric response function, ε. In the case of such samples there is no grain boundary scattering. In thin films, grain boundaries are introduced and electron scattering at these boundaries influences the measured values of ρ and ε. Recent work addressing grain boundary scattering in thin films extends, for example, from investigations of the electrical properties of Cu films [6] (motivated by increased usage in integrated circuitry) to the optical properties of polycrystalline Au films [7]. In the investigation reported here the optical response of a polycrystalline Au film and single crystal, bulk Au is examined in detail at wavelength 3.392 μm using a highly sensitive surface plasmon polariton (SPP) technique at ambient temperature and at ∼100 K. The combination of these different samples at different temperatures in a direct, highly sensitive comparator study distinguishes this work from the considerable body of literature on the optical properties of gold (relevant aspects are briefly reviewed below) and allows us to assess the relative contributions of electron–phonon scattering and electron–grain boundary scattering to the optical data and, indeed, to comment on electron–electron scattering in the low energy regime.

In parallel to past experimental work where surface and grain boundary scattering clearly have an influence on the results, there has been a variety of theoretical developments describing the scattering processes. The problem of surface scattering was first tackled by Fuchs [8] and later by Sondheimer [9], Chambers [10] and Soffer [11]. However, while these surface scattering theories can successfully explain aspects of thin film resistivity measurements there are shortcomings that are remedied on two fronts principally. Firstly, they do not address grain boundary scattering, a phenomenon tackled in the model of Mayadas et al. [12,13]; secondly they are classical models and must give way to quantum transport models [14–16] in certain circumstances, e.g. very thin films (thickness on the scale of the Fermi wavelength) and at very low temperatures. The various models have been applied with some success in the interpretation of d.c. resistivity measurements in the context of both thin films (e.g. Cu [6] and CoSi$_2$ [17]) and polycrystalline Au nanowires [18]. Recently, also, the Mayadas and Schatzkes (MS) model has been extended to the optical regime [7] and applied to measurements of the reflectance of gold films across a broad spectral range; the formula connecting to d.c. resistivity is recovered in the long wavelength regime.

The optical properties of gold have been studied extensively over the past several decades. Aspnes et al. [19] give a good outline of such investigations up to the start of the 1980's-these included the examination of annealed/unannealed thin/thick film samples and bulk samples using a variety of techniques such as the measurement of direct reflectance, combined reflectance and transmittance and ellipsometry. Of these investigations only a few measure both bulk and thin (or thick) film samples [20–25]. The principal issue addressed in the work of Aspnes et al. [19] was the resolution of discrepancies between different sets of optical data, especially in the energy range above ∼2.5 eV. Since 1980 there have been further investigations of deposited gold films [7,26–31]. These have ranged, for example, from an examination of the optical properties resulting from different growth conditions [26] and as a function of subsequent annealing [27]. Other investigations have