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Extracting the Ag surface and volume loss functions from reflection electron energy loss spectra

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ABSTRACT

Reflection electron energy loss spectra have been measured for silver using incoming electrons with energies between 5 and 40 keV, in a surface and volume-sensitive geometry. Bulk and surface loss functions are extracted from these data and various consistency checks are applied to the obtained loss functions. Depositing minute amounts of Al onto the Ag surface causes a severe reduction in surface features. The intensity of the surface feature seems now to increase as the probe energy is increased. A mechanism by which this can occur is discussed. The relation between the bulk loss function and the dielectric function is discussed, and a comparison with the results of transmission electron energy loss spectra and optical data is made.

1. Introduction

Reflection electron energy loss spectroscopy (REELS) has attracted interest for over 50 years [1]. It was established early that the spectra contain information about surface and volume loss features [2,3], and that there is a close relation between these features and the dielectric function of the material. Knowledge of the dielectric function is important, not only to describe the interaction of photons and energetic electrons with a material, but also for the description of electron–electron correlation effects in ab initio calculations, as the electron–electron interaction is effectively reduced by screening due to the medium, and this reduction is described by the dielectric function. Experimental information about the dielectric function is thus extremely important.

However, extracting the dielectric function from a REELS spectrum turns out to be a real challenge and has attracted a lot of theoretical interest [4,5]. A main hurdle is that simultaneous understanding of both surface and bulk loss processes is required and this problem has been addressed in several papers in the last few years (see e.g. [6–10]). It has even been suggested that at the lowest energies interference between volume and surface oscillations will make separation impossible [5,11,12], and a REELS spectra cannot be considered to be a simple linear combination of surface and volume components. We assume that this problem does not occur in the present measurements which are at relatively high energies (5 keV and above).

Silver is a ideal material for study as the REELS spectrum is feature-rich and contains a very strong peak in the vicinity of 3.7 eV, which is due to both surface (3.63 eV) and volume (3.78 eV) plasmons. These surface plasmon features play an important role in the development of plasmonic devices [13,14]. Surface and volume plasmons were resolved in high-resolution transmission measurements [15], but reflection electron energy loss measurements usually lack the required resolution. While our current experimental resolution prohibits us from resolving the two components individually, by changing the energy and geometry of the incident electrons we are able to reduce or enhance either contributions. At larger energy loss values there is second plasmon near 8 eV followed by additional structure due to interband transitions.

At an interface a different loss mode is possible. For a free electron material the interface plasmon is at an energy

$$\omega_i = \frac{\omega_{\mathrm{pl}}}{\sqrt{1+\epsilon}}, \qquad (1)$$

with ω_{pl} the plasmon energy and ϵ the dielectric constant of the overlayer material [16]. For a surface the dielectric constant is that of the adjacent vacuum ($\epsilon = 1$) and the surface plasmon is at $\frac{1}{\sqrt{2}}\omega_{\mathrm{pl}}$. As noticed before for silver the bulk and surface plasmon are much closer in energy than these values, due to the influence of the 4d bands. Daniels studied the influence of a carbon overlayer on Ag [17]. Near the Ag plasmon energy the dielectric constant of carbon is >1, and the surface plasmon shifts to lower energy loss values after carbon deposition (and becomes much more strongly damped). Here, we investigate what happens, if we deposit aluminum on an silver surface. Near 4 eV the Al dielectric function is

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severely negative, and $1+\epsilon$ becomes negative and the imaginary value of ω_i in Eq. (1) suggests that no interface plasmon will exist.

The surface excitation parameter (SEP) is the average number of surface excitations an electron experiences in crossing the vacuum–solid interface once. The SEP for medium-energy electrons is given in Ref. [18] as

$$P_\mathrm{s}(\theta, E_0) = \frac{a}{\sqrt{E_0}\cos\theta}, \tag{2}$$

where E_0 is the incident electron energy, θ is the angle of the surface crossing with respect to the surface normal and a is a material parameter, being equal to $2.896\,\mathrm{eV}^{1/2}$ for free electron materials. Thus one can change the probability of exciting a surface plasmon by either changing the probe electron energy or by changing the angle of incidence of the incident beam to the surface. It is this property that enables to distinguish between volume and surface features of the energy loss spectra. As the excitation probability scales as $1/\sqrt{E_0}$ one has to increase the energy 4-fold to get a reduction of a factor of 2 of the fraction of detected electrons that experienced surface losses.

Note that the surface (and interface) plasmons are not purely an additional loss feature. Already the early theory by Ritchie [3] predicted a corresponding decrease in the excitation probability of a bulk plasmon near the surface, that was recently demonstrated by analysis of experimental REELS [19]. The width of the surface scattering zone is given by v/ω_s [3], where v is the speed of the electron as it crosses the surface and ω_s is the surface plasmon frequency. As a consequence, the depth over which the bulk plasmon excitation is reduced due to the surface, increases with the square root of the energy. The thickness of the overlayer required to replace the surface plasmon by an interface plasmon increases with energy as well [16].

In the past theory and experiment were confronted with each other using Monte Carlo simulations, reconstructing the experiment and using theoretical estimates of the loss functions etc., as an input. For example, in an extensive study Ding et al. [20] compared theoretical depth-dependent loss function with experimental REELS spectra using Monte Carlo simulations. They identified another surface loss feature, besides the sharp loss feature near 3.7 eV. This feature, near 7.5 eV, is much broader in energy, but also displays a maximum in cross section at the surface.

Recently, a new scheme was developed to determine the single scattering surface and volume loss functions directly from the experimental data [21]. This calculation requires as input two loss spectra for which the contributions due to surface and volume loss functions are different, for example loss functions measured at different energies and or geometrical configurations. The technique involves deconvoluting the loss function to remove multiple scattering while simultaneously separating surface and volume components. This method was successfully applied to Ag and Au using high-energy REELS data from the spectrometer at the Australian National University [22,23]. This spectrometer can be used to measure REELS spectra in an energy range between 5 and 40 keV, and is hence ideally suited to provide the input data for the extraction of the surface and volume excitation function by the aforementioned theory. Further the complex dielectric function was derived from the volume and surface loss function, by fitting it with a set of Drude–Lindhard oscillators [23]. The dielectric function obtained in this way satisfies Kramers–Kronig relation and the bulk loss function is given by $\mathrm{Im}\{-1/\epsilon\}$ and the surface loss function by $\mathrm{Im}\{(\epsilon-1)^2/\epsilon(\epsilon+1)\}$. The REELS-derived dielectric function appeared to be in better agreement with density-functional theory calculations than the dielectric function obtained by optical means [24].

The method developed by Werner to derive the loss functions from a REELS spectrum is far from trivial. If it can be validated then REELS can become an important tool to derive dielectric functions over a wide energy range, and a large variety of samples. Thus, it is highly desirable to be able to judge the validity of the obtained surface and volume loss functions by experiments. This paper tries to explore to what extent this is possible for the case of silver, by studying the effects of changing energy and geometry, as well as the influence of adding a thin overlayer to silver.

2. Experiment

The measurements presented in this work were performed on the high energy electron spectrometer at the Australian National University, shown in Fig. 1. The electron energy analyzers have been described in detail elsewhere [25] and are operated at a pass energy of 200 eV. Measurement can be done with either gun A or gun B. Both guns are equipped with a BaO cathode, operating at low temperatures to minimize the energy spread. The cathode is held at a potential of −500 V. The sample is positioned in a high voltage hemisphere which is held at the required voltage (ie., 4.5, 9.5, 19.5 and 39.5 kV). Thus electrons with an energy of 5, 10, 20 and 40 keV are incident on the target. Electrons which scatter from the target are decelerated and focussed into the entrance of a hemispherical electron energy analyzer. Ripple and drift of the main high voltage power supply do not affect the resolution of the experiment, as it is used both to accelerate the incoming electrons and decelerate the scattered electrons, and hence does not change the energy of the detected electron inside the hemispherical analyzer. The analyzer is held at a (comparatively low) voltage such that electrons with the desired energy pass through the analyzer and are detected by a pair of micro-channel plates followed by a resistive anode. facilitating two dimensional analysis of the electron position. Electrons over an energy range of 30 eV can be detected simultaneously and analyzed accurately for their energy. The combined resolution of gun and analyzer is always better than 0.5 eV.

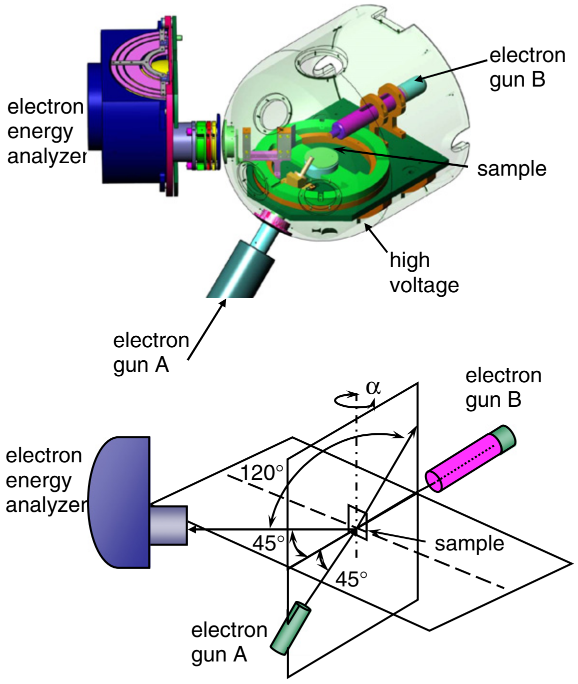

Fig. 1. Outline of experimental apparatus (top). Schematic of the experiment showing the relative positions of the two electron guns and sample position (bottom). The sample can rotate around the vertical axis over an angle α. For the sample orientation drawn here $\alpha = 0°$.