Reflectivity Anisotropy Spectra of Cu- and Ag- (110) surfaces from \textit{ab initio} theory

Patrizia Monachesi*, Maurizia Palummo, Rodolfo Del Sole
Dipartimento di Fisica - Università di Roma, 'Tor Vergata' and Istituto Nazionale di Fisica della Materia I-00133 Roma, Italy

Rajeev Ahuja and Olle Eriksson
Condensed Matter Theory Group, Physics Department, Uppsala University, S-7512 Uppsala, Sweden

We present the surface Reflectivity Anisotropy spectra of the relaxed (1x1) (110) surface of Cu and Ag as obtained by \textit{ab initio} calculations. We are able to disentangle the effects of the intraband and interband parts of the bulk dielectric function on the bare dielectric anisotropy of the surface. We show how the position, sign and amplitude of the structures observed in such spectra depend on the above quantities. The lineshape of all the calculated structures agree very well with the ones observed experimentally for samples treated by suitable surface cleaning. In particular, we reproduce the observed single peak structure of Ag at high energy, found to represent a state of the clean surface different from the one giving the originally observed double peak structure. This results is not reproduced by the ‘local field’ model.

The Reflectivity Anisotropy Spectroscopy (RAS) is a powerful technique to probe the optical properties of an anisotropic medium like the surface of an otherwise isotropic bulk crystal. The RAS is measured as the relative difference \( \Delta r \) of the complex reflectivity \( r \) along two perpendicular axes on the surface. Despite its vast application in semiconductors, surface science since the pioneering work by Aspnes, the first RAS spectrum of a metallic surface appeared as late as in 1993 for the Ag (110) surface. The characteristic resonance-like structure at the bulk plasma frequency, i.e. at \( \omega_p \approx 3.8 \text{ eV} \), has been considered a fingerprint of the Ag-(110) surface. More recently, the research on the optical properties of metallic surfaces has gained renewed impulse and in the last three years the (110) surface of Ag and Cu have been investigated both by optical and photoemission spectroscopy.

The RAS results essentially agree in establishing the existence of one peak at low energy (< 2.5 eV) of similar shape in both Cu and Ag and of a further structure at higher energy of quite different shape. In particular, some authors point out that the lineshape of the high-energy peaks depends critically upon the surface treatment during the sample preparation. This experimental aspect is very important for a correct comparison of RAS spectra with theoretical models and calculations.

A major problem with the interpretation of the RAS spectra is that the optical anisotropy introduced by the surface is difficult to extract from the measured reflectivities without a solid quantitative theoretical basis. An attempt to do so has been made from a phenomenological point of view. Experimentally one can observe the evolution of a given feature in the spectra from the clean to the gas-covered surface. In fact coverage by, e.g., oxygen, is known to wash out progressively optical structures originating from surface-to-surface state transitions, as a function of time and/or amount of oxygen.

RAS structures observed in the noble metals are currently interpreted in terms of interband transitions between surface or bulk states by speculating on available results of existing band structure obtained by folding bulk bands or by interpolation methods. Another tool of interpretation is the so-called ‘swiss cheese’ model, describing the optical response of the surface by layer-depending dipolar interactions. This phenomenological model partially succeeds, at least qualitatively, to explain the RAS peaks observed in Ag and Cu under suitable experimental conditions. The lineshape, however, depends on the parameters of the model. Only very recently first principle calculations of the optical properties of noble metals surfaces have started to appear, opening the possibility of a direct quantitative interpretation of the measured optical spectra. Such self consistent calculations yield, on the same footing, the electronic structure and the dielectric functions \( \epsilon_{[1\overline{1}0]} \), \( \epsilon_{[001]} \) along the directions [1\overline{1}0] and [001] of the (110) surface. The dielectric function is computed from interband transitions among electronic states. From these, the \( \Delta \epsilon = \epsilon_{[1\overline{1}0]} - \epsilon_{[001]} \), known as Surface Dielectric Anisotropy (SDA), is derived. So far, comparison of the calculated SDA with direct experimental RAS results is made through a reliable semi-phenomenological model that transforms the RAS spectrum into the SDA via the bulk dielectric function \( \epsilon_b \) normally obtained by independent measurements. Attempts to interpret the RAS spectrum in terms of bulk or surface electronic transitions from the SDA structures may, however, be incorrect. In fact, the passage from the anisotropic dielectric function to the RAS spectrum involves bulk quantities that re-shape much of the bare metallic SDA spectrum. At low energies, as shown below, RAS and SDA have different signs due to intraband transitions, at variance with the case of semiconductors. This
point is even more important in view of recent controversial results for the sign of the RAS\(^{12}\) Therefore, as we aim to show in this Letter, only the calculation of the RAS spectrum from consistently computed quantities allows to distinguish between RAS structures arising from the bare SDA from those related to bulk effects.

We shortly summarize the fundamental analytical expressions necessary for the analysis of a RAS spectrum. The surface reflectivity anisotropy \(\frac{\Delta r}{r}\), written for the present surface geometry, is \(\frac{\Delta r}{r} = 2\tau_{[\overline{0}01]}^{-\tau_{[001]}}\). The RAS spectrum, as obtained directly from reflectivity measurements, is usually given as the real part of the above complex quantity, namely:

\[
Re\left\{\frac{\Delta r}{r}\right\} = C(\frac{\Delta \epsilon_2 (\epsilon_1^1 - 1)}{(\epsilon_2^1 - 1)^2 + (\epsilon_2^1)^2} - \frac{\epsilon_2^1 \Delta \epsilon_1}{(\epsilon_1^1 - 1)^2 + (\epsilon_2^1)^2}),
\]

where subscripts 1, 2 refer to the real and imaginary parts, respectively and C is a constant that is of no importance here.

In metals, all the \(c\)’s in the formula above contain terms due to interband as well intraband transitions. The latter ones give rise to the so-called Drude tail dominating at low energies. We assume that the anisotropy of the intraband part of \(\Delta \epsilon\) is negligible, which allows us to neglect intraband effects tout court\(^{13}\) in this term. In fact there is, so far, some experimental evidence\(^{13}\) that the intraband anisotropy of the surface affects the spectrum of Cu only up to 1.5 eV. The inclusion of intraband effects in \(\epsilon^b\) is, instead, of paramount importance, as we will show below. Therefore our calculations contain the \textit{ab initio} computation of the interband part of all the surface and bulk \(c\)’s plus the inclusion of the Drude tail in \(\epsilon^b\) computed by the standard relations involving the plasma frequency \(\omega_p\) and the relaxation time \(\tau\) of the bulk metal\(^{14}\).\(^{13}\)

The computation of \textit{ab initio} quantities, i.e., electronic properties and intraband part of the dielectric functions, has been carried out self-consistently\(^{10}\) by the Full Potential version\(^{10}\) of the Linear Muffin Tin Orbital method\(^{10}\) within the Local Density Approximation\(^{15}\) for the exchange and correlation potential.\(^{10}\) The surface geometry is obtained within a repeated slab scheme including 11 atomic plus 6 vacuum layers. The reciprocal space integrations are performed with the analytical tetrahedron method\(^{16}\). Meshes as dense as 752 and 256 k-points in the irreducible bulk and surface Brillouin Zone, respectively, give converged values for the dielectric functions calculated as matrix elements of the momentum operator among occupied and unoccupied electronic states. The relaxed\(^{10}\) unreconstructed geometry of the Cu and Ag (110) surfaces\(^{10}\) has been taken into account. A more complete description of the details of the calculations will be published in a future work.

In Fig. 1 and Fig. 2 we have plotted the calculated RAS, \(Re\{\frac{\Delta r}{r}\}\) and SDA, \((\epsilon_{[\overline{0}01]} - \epsilon_{[001]}\), for Cu and Ag, respectively. To disentangle the effect of the intraband from interband part of \(\epsilon^b\) in the RAS we have also plotted in the upper panel of Fig. 1 and Fig. 2 \(Re\{\frac{\Delta r}{r}\}\) calculated without the intraband (Drude) term in \(\epsilon^b\). In Fig. 3 we show the plots of the calculated real and imaginary part of \(\epsilon^b\), separated into total and interband parts, for bulk Cu (upper panel) and Ag (lower panel). The plots shown in these figures illuminate very clearly that in both metals, the overall effect of \(\epsilon^b\) is to re-shape profoundly the bare dielectric anisotropy of the surface \(\Delta \epsilon\), depending on the energy and on the peculiarities of the bulk dielectric function of each metal. The RAS spectra of the two metals may be divided into a low (<2.5 eV) and high (between 3 and 5 eV) energy part, according to the prominent spectral features. The low energy peak has a similar shape in both metals whereas the high energy structure looks quite different.

Let us now focus on the two metals separately in order to highlight how characteristic quantities of the bulk, e.g. the plasma frequency, affect the RAS spectrum. In Fig. 1 (upper panel) the RAS spectrum of Cu, with and without the Drude term in \(\epsilon^b\) may be compared with the SDA in the lower panel. From this one sees very clearly that the low energy peak in the SDA undergoes a sign reversal and a little energy shift due to the intraband part of \(\epsilon^b\). This effect decreases with increasing energy until the interband part of \(\epsilon^b\) takes over. For energies larger than \(\approx 5\) eV the effect of the Drude tail dies off almost completely. The double peak shape of the high energy structure is essentially determined by the interband part of \(\epsilon^b\) between 4 and 5 eV (see Fig. 1, upper panel) whereas the Drude part of \(\epsilon^b\) amplifies the negative part of this peak between 4 and 4.5 eV.

In Ag the effect of \(\epsilon^b\) is even more dramatic, as can be seen from the two curves in the upper panel of Fig. 2, by comparing them with the SDA plot in the lower panel. The low energy part of the spectrum (see the inset of Fig. 2) is determined by the same interplay of bulk intraband \(\epsilon^b\) and SDA as observed in Cu. The RAS spectrum is, however, dominated by the effect of the bulk plasmon producing the overwhelming negative structure at about \(3.2\) eV. This is due to the steep behaviour of \(\epsilon^b\) close to the treshold of the onset of the interband transitions, as can be inferred from Fig. 2 (lower panel). Afterwards, the spectrum is only slightly affected by the Drude term, as in the case of Cu.
Let us now come to the direct comparison of our calculated RAS spectra with the corresponding experimental ones. As pointed out very clearly by extensive studies, the lineshape of the observed structures may vary drastically not only upon exposure in air but also upon the number of cleaning cycles of the surface.

RAS spectra of Cu and Ag clean (1x1) (110) surface have been measured by various groups in different experimental conditions. All these spectra display the low energy peak at \( \simeq 2.1 \) and 1.8, in Cu and Ag, respectively and the high energy structure located between 4 and 5 eV, in agreement with our findings above. However, the shape of the latter structure depends upon treatment of the surface. In particular, a recent paper on the effect of sputtering on the RAS spectrum of the (110) surface of Cu shows that the shape of the double-peak structure at high energy (see Fig. 1) varies very much with sputtering, holding as fixed the ‘node’ of the structure (see Fig.1 of Ref.6). This node occurs also in our calculations at essentially the same energy. We emphasize that the position and overall shape of the two structures in the RAS of Cu presented in this letter agree quite satisfactorily with the experimental results.

Also for the Ag clean (1x1) (110) surface our calculated RAS spectrum in Fig 2 gives satisfactory agreement with the experimental findings apart from the shift of about 0.5 eV toward lower frequency in the location of the high energy structure. We attribute this discrepancy to the value of the threshold of the interband transitions that amounts to 3.3 eV in our calculations, as can be seen in Fig. 3 (lower panel). This value is 0.5 eV smaller than the experimental one. (This discrepancy has been found also in another calculation for bulk Ag, carried out using the pseudopotential method; it must be due to the shortcoming of Density Functional Theory, that sometimes underestimates transition energies.) The lineshape of this structure is surprisingly in agreement with the one obtained in very intensively polished samples, as discussed above. The double peak, resonance-like structure measured in freshly polished Ag surface, instead, does not occur in our \textit{ab initio} calculations, since they do not include the long-ranged local-field effect. This is described by the 'swiss-cheese' phenomenological model where the noble metal is modeled by a composite medium made by a jellium-like background (the sp electrons) screening the embedded charged spheres, centred about ions carrying dipoles (due to the d electrons) interacting among themselves. The effect of the reduced symmetry of the surface on the dipole-dipole interaction leads to different plasma frequencies for the different light polarizations. This is the origin of the derivative-like lineshape observed in Ag RAS at high energy. Its absence at surfaces treated by several sputtering cycles may be understood by the introduction of defects (\textit{e.g.} vacancy islands) by the treatment itself. The geometrical roughening of the surface may destroy the long range order, suppressing the effect of dipolar interactions and leaving only the dominant effect of the local environment, well described by our one-electron calculations.

To conclude and summarize, we have in this Letter calculated \textit{ab initio} the RAS spectra of Cu and Ag (110) surfaces, showing which structures are due to the surface dielectric anisotropy and which are due to bulk effects. Moreover we have disentangled intraband from interband contributions of the bulk dielectric function in the RAS spectrum, showing that it is incorrect to interpret RAS spectra from the knowledge of the SDA only. For the first time the RAS structures observed at metal surfaces have been accurately reproduced by \textit{ab initio} calculations. The measured lineshapes in the Cu and Ag RAS depend critically on the conditions of the surface. As discussed extensively in some papers, sputtering, annealing or exposure in air may change not only the amplitude but also the shape of the structures as found for the high energy peaks in Cu and Ag. We conclude that our results and those obtained by the local-field model refer to samples whose surface conditions emphasize short-range and long-range arrangements of the atoms on the surface, respectively.

*On leave from Dipartimento di Fisica - Universitá dell’Aquila, I-67100 L’Aquila (Italy)*

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FIG. 1. RAS (upper panel, solid line) and SDA (lower panel) spectra for the Cu-(110) surface. The dotted curve in the upper panel is the RAS obtained excluding the Drude tail from $\varepsilon^b$. 

FIG. 2. The same plots as in Fig. 1 for the Ag-(110) surface. The inset shows the low energy peak on a magnified scale.

FIG. 3. Calculated Real and Imaginary parts of $\varepsilon^b$ for Cu (upper panel) and Ag (lower panel): total (bold full line) and interband (dotted line) $\varepsilon^b_1$, total (dashed line) and interband (dash-dotted line) $\varepsilon^b_2$. The bulk free-electron $\omega_p$ and relaxation time $\tau$ are taken from Ref. 11 to be 9.17 eV, $6.9 \times 10^{-15}$ sec$^{-1}$ and 9.22 eV, $31 \times 10^{-15}$ sec$^{-1}$ for Cu and Ag, respectively.
$\Re(\Delta r/r)$

$\Im(\varepsilon_{[1-10]} - \varepsilon_{[001]})$
