# Electronic properties of gold thin films studied by electron energy loss spectroscopy

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## Abstract

**High-resolution electron energy loss spectroscopy was used to investigate the electronic properties of (111)-oriented Au ultrathin films grown on Cu(111). The loss spectrum showed several features which were ascribed to both single and collective excitations. In particular we distinguished features assignable to dispersionless single-particle transitions and the dispersing electron-hole continuum as well as the ordinary and s-like surface plasmon, and the multipole surface plasmon.**

**Keywords:** electron energy loss spectroscopy (EELS), gold films, surface plasmons

## Introduction

Nanoscale thin films are attracting a considerable interest in recent years for both fundamental interest and technological applications [1-7]. They are a unique class of nanosystems, whose electronic properties can be easily tuned upon controlling the thickness of the film at the atomic level. This interest is motivated by the lack of information on such systems compared with bulk crystals and by the broad potential applications in nanoelectronics and nanocatalysis. Gold systems, such as semi-infinite media [8], thin films [9], quantum wires [10, 11], and nanoparticles [12] have been extensively studied as a consequence of the discovery that Au is a selective catalyst for a variety of important chemical reactions [13-18]. However, little is known about the coexistence and the possible interplay between single-particle and collective excitations in thin Au films. On the other hand, electronic excitations play an important role in the reactivity of metallic systems. Hence, understanding the electronic properties of gold films could lead to the tailoring of more selective catalysts and to the improvement of the existing ones. Moreover, studies on noble-metal systems are particularly motivated by fundamental interest. In fact, the presence of localized d electrons makes unrealistic the jellium model usually applied for describing dynamic screening of simple metals. Several attempts have been undertaken in order to include band-structure effects in theoretical models [19, 20].

Herein we report on high-resolution electron energy loss spectroscopy (HREELS) measurements on the electronic properties of gold thin films deposited at room temperature on Cu(111).

The loss spectrum showed several features. Besides the Au surface plasmon (SP) at about 2.6 eV, low-energy single-particle transitions were revealed too. A broad peak at about 6 eV was assigned to contributions from both the s-like Au SP and the Au multipole surface plasmon (MP). Off-specular HREEL spectra revealed the existence of a loss tentatively assigned to the continuum of electron-hole pair excitations.

## Experimental

Measurements were carried out in a UHV chamber operating at a base pressure of $5 \cdot 10^{-9}$ Pa. The sample was a single crystal of Cu(111). The surface was cleaned by repeated cycles of ion sputtering and annealing at 700-800 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Gold was deposited onto the Cu(111) surface by evaporating from an Au wire wrapped on a tungsten filament. In order to prepare flat Au films with a limited roughness (which is an important parameter as it allows coupling between light and the SP), reflectivity measurements using the electron impinging beam in specular

geometry (dipole scattering) were performed for various deposition conditions. Such measurements demonstrated that a smooth surface with a negligible roughness could be achieved under optimized deposition parameters. In particular, highly-reflective and well-ordered flat Au films could be obtained at very low deposition rates (≈0.05 ML/min). The occurrence of the p(1x1)-Au LEED pattern was used as the calibration point of $\theta_{Au}$=1.0 ML. Similar results were obtained by a calibration procedure using AES. A constant sticking coefficient was assumed to obtain other desired Au coverage. The flatness of the Au film is also ensured by LEED and SP dispersion measurements. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The incident angle with respect to the sample normal was fixed at 55.0°. The acceptance angle of our spectrometer is ±0.5°. The energy resolution of the spectrometer was degraded to 10 meV so as to increase the signal-to-noise ratio of loss peaks. Dispersion of the loss peaks, i.e., $E_{loss}(q_{||})$, was measured by moving the analyzer while keeping the sample and the monochromator in a fixed position. To measure the dispersion relation, values for the parameters $E_p$, impinging energy and $\theta_i$, the incident angle, were chosen so as to obtain the highest signal-to-noise ratio. The primary beam energy used for the dispersion, $E_p$=92 eV, provided, in fact, the best compromise among surface sensitivity, the highest cross-section for mode excitation and $q_{||}$ resolution.

As

$$\hbar \vec{q_{||}} = \hbar \, (\vec{k_i}\sin\theta_i - \vec{k_s}\sin\theta_s),$$

the parallel momentum transfer, $q_{||}$ depends on $E_p$, $E_{loss}$, $\theta_i$ and $\theta_s$ according to:

$$q_{||} = \frac{\sqrt{2mE_p}}{\hbar} \, (\sin\theta_i - \sqrt{1 - \frac{E_{loss}}{E_p}} \, \sin\theta_s)$$

where $E_{loss}$ is the energy loss and $\theta_s$ is the electron scattering angle [20].

Accordingly, the integration window in reciprocal space [21-23] is

$$\Delta \, q_{||} \approx \frac{\sqrt{2mE_p}}{\hbar} \, (\cos\theta_i + \sqrt{1 - \frac{E_{loss}}{E_p}} \, \cos\theta_s) \, \alpha$$

where $\alpha$ is the angular acceptance of the apparatus. The integration window in the reciprocal space for SP dispersion measurements was estimated to be 0.024 Å$^{-1}$, much less than the scanned range in the reciprocal space.

All depositions and measurements were made at room temperature, at which no trace of AuCu alloy was revealed in both LEED and AES measurements.

# Results

The HREEL spectrum acquired in specular geometry for a thin Au film (10 layers) on Cu(111) is dominated by the SP at 2.61 eV (Figure 1), in agreement with optical [24-27] and scanning tunneling spectroscopy [8, 28] measurements.

Interestingly, for gold $\varepsilon_1$= -1 (which is the condition for the existence of a SP) occurs at 3.0 eV [29], but in the Au loss spectrum there is no peak at such energy. Moreover, for Au the interband transition onset at 2 eV [29] lies below the energy of SP, thus the SP peak is expected to be less distinct compared with Ag, for which the opposite occurs [30]. As a matter of fact, the Au SP has a full-width at half maximum (FWHM) of about 0.6 eV at small momenta and it dispersed up to 1.6 eV as a function of parallel momentum transfer [31]. In comparison, the FWHM of the SP in Ag thin films grown on Cu(111) is about 0.3 eV [32].

Besides the Au SP, also a sharp peak at 0.67 eV (top panel of Figure 1) and a broad feature at about 6 eV (bottom panel) were revealed. Concerning the latter peak, it could be ascribed to another SP. In fact, $\varepsilon_1$= -1 also for energies around 5-6 eV [29], so as to suggest the occurrence of plasmonic modes confined at the surface. It is worth mentioning that for a jellium surface with a density $r_s$=3, i.e. the effective radius for Au, the SP should have an energy of 6.40 eV [33]. The presence of d-electrons shifts the ordinary SP energy down to 2.50 eV [8, 24-28, 31]. Hence, we assign the peak at 6 eV to the s-like SP of Au. A similar excitation was found at about 7 eV in Ag films on Cu(111) [34]. According to theoretical findings [35], such peak has both s-like monopole and multipole SP components which could not be separated. We argue that a similar mechanism occurs for Au.

The behavior of the peak at 0.67 eV deserves a remarkable consideration as, because of its low energy, it should influence the decay rate of all electronic excitations at the metal surface and thus chemical reactions [36].

Beside the feature at 0.67 eV, another peak at 1.53 eV was recorded. However, the peak at 0.67 eV is accessible only in scattering geometries near to the specular condition, thus ensuring of its dipolar nature [20]. On the other hand, the feature at 1.53 eV is recorded only in off-specular spectra, very likely due to its impact character. Changing the scattering geometry could open new excitation channels. This finding indicates the interplay between different single-particle excitations in Au thin films.

A careful inspection of the HREEL spectrum of the top panel of Figure 1 revealed also the existence of a dispersionless feature at 0.37 eV. Its energy is too high to be assigned to phonons or vibrations. The absence of any dispersion prevents from its assignment to a plasmonic excitation. Hence, we ascribe it to another single-particle transition.

The Au SP instead exhibits a clear dispersion of its frequency with the scattering angle. (top panel of Figure 1). Figure 2 shows the SP dispersion for a thin film of Au on Cu(111) (10 ML) compared with the case of a thick Au film on the

same substrate, whose SP dispersion as been studied in Ref. 31. The dispersion of the Au SP was found to be positive in both cases. A similar result was reported for Ag systems [5, 20, 33, 37]. According to the Feibelman's model [38, 39] of the SP dispersion, this implies that the position of the centroid of the induced charge, $d^{\perp}$, lies inside the geometrical surface ($z < 0$), as for Ag [40]. On the other hand, according to Liebsch's model [41], the position of the centroid of the induced charge is always external with respect to the jellium edge. Hence, the positive dispersion of the SP is due to the

stronger influence of the polarizable medium when the penetration depth of the SP is larger.

The dispersion relation of Au SP could be in principle influenced by band-structure effects as a consequence of the presence of d-electrons [42-44].

It is worth noticing that the SP frequency in the long wave-length limit (small momenta) is increased by about 50 meV in thin Au films with respect to thick adlayers [31]. The blue-shift of the SP frequency was previously observed in thin Ag films on Si(111) [37] and Cu(111) [32] and it is fully described within the framework of s-d polarization model [19]. As the thickness of the Au film is reduced, the overall screening of the charge associated to the SP via the polarizable d electronic medium diminishes, giving a higher plasmon energy. Furthermore, the spill-out region not affected by s-d polarization becomes more important, causing a further blue-shift of the plasmon frequency. However, at higher momenta the SP frequency is similar in thin and thick Au film.

The lower slope of the Au SP dispersion relation in thin Au film compared with the thick film could be ascribed to the minor penetration of the centroid of the induced charge inside the bulk [38, 39].

Moreover, the absence of a plateau in the SP dispersion [32, 45] further ensures of the flatness of the Au film. In fact, the existence of islands within the film should imply the confinement of the SP, indicated by the lack of any dispersion for SP frequency up to a critical wave-vector related to the island size.
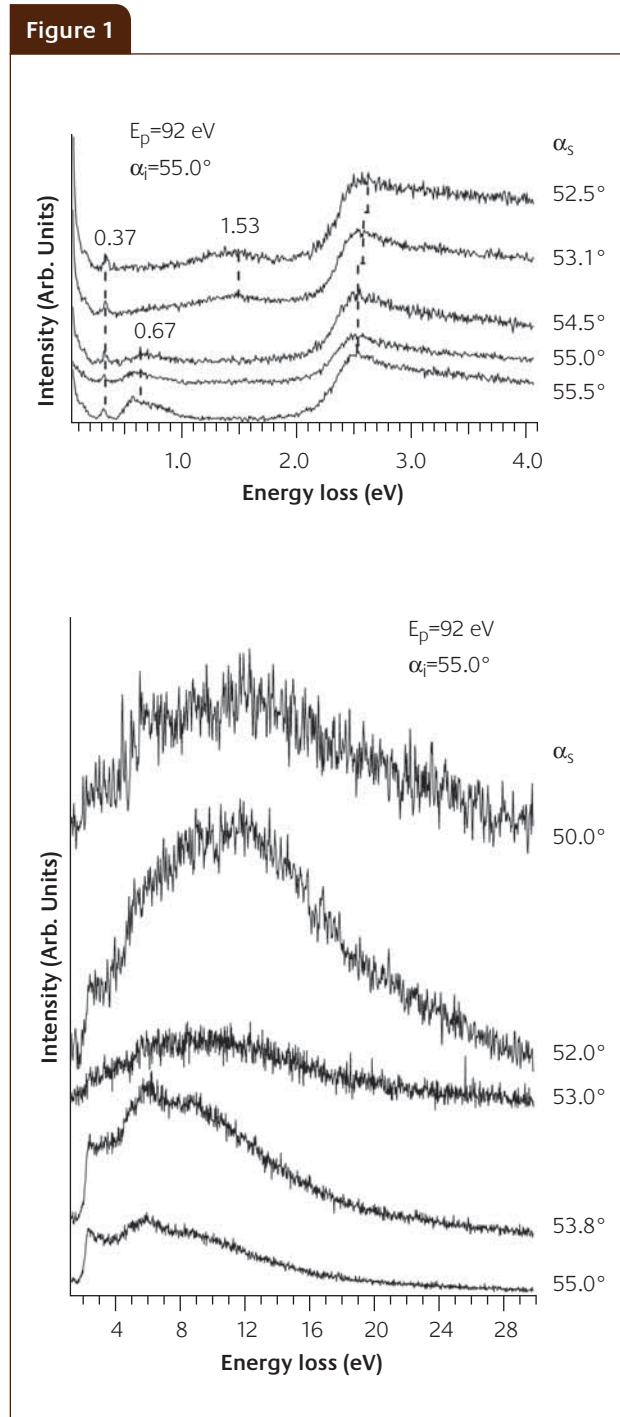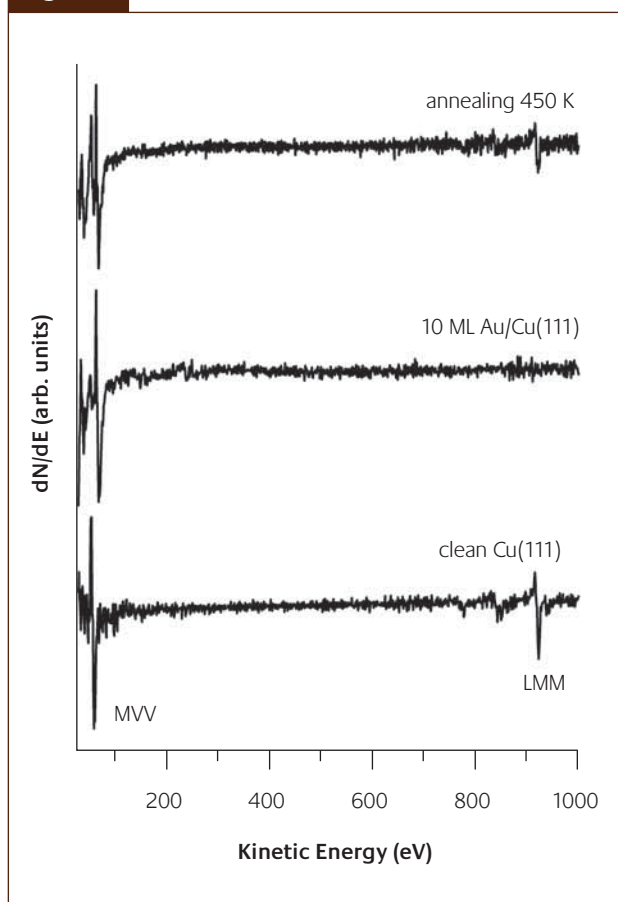
**Figure 1**



*HREEL spectra as a function of the scattering angle in a restricted (top panel) and wider range (bottom panel)*
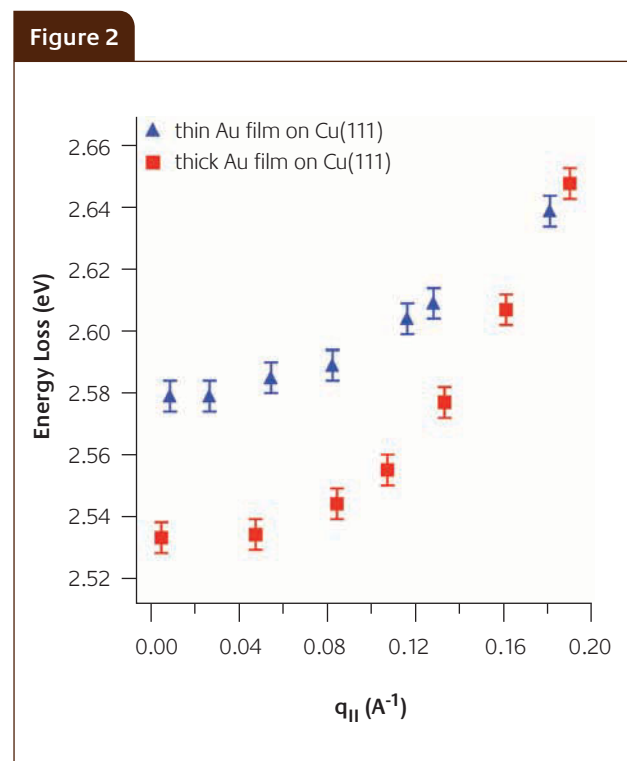
**Figure 2**



*SP dispersion for a thin (present results) and a thick (data taken from Ref. 31) film of Au on Cu(111)*
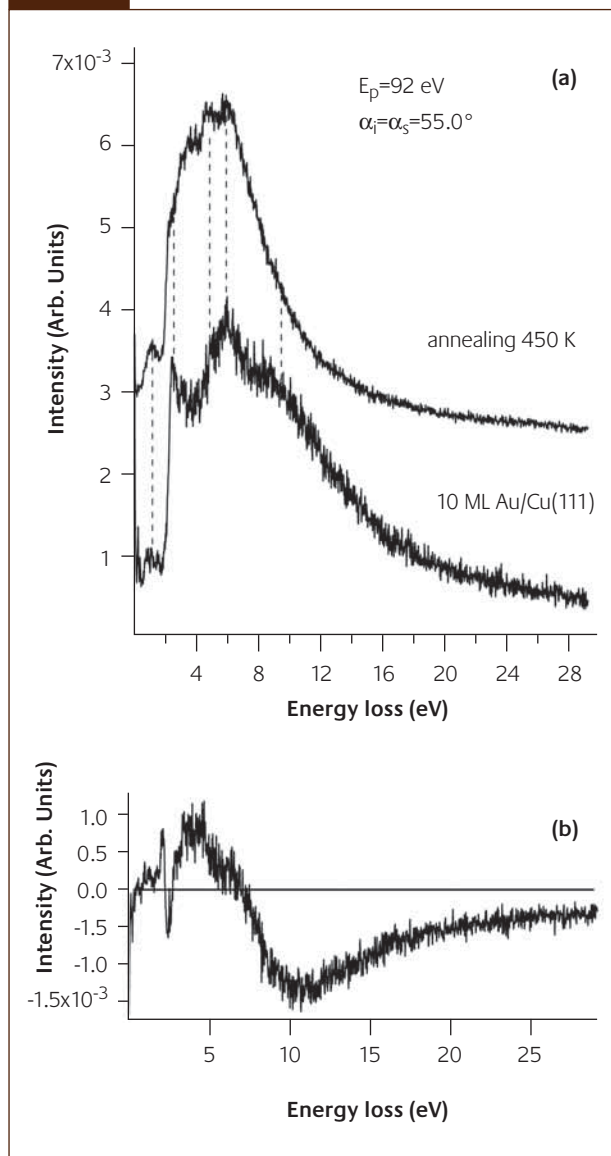
**Figure 3**



*AES spectrum for the Cu(111) substrate, 10 ML Au/Cu(111) and the Au-Cu alloy*

**Figure 4**



*(a) HREEL spectra for 10 ML Au/Cu(111) and the Au-Cu alloy;*
*(b) Difference spectrum*

On the contrary, the peak at about 6 eV does not exhibit any dispersion (bottom panel of Figure 1); it reaches the maximum intensity at 2° off-specular and suddenly disappeared by increasing the off-specular angle as a consequence of the opening of new excitation channels via interband transitions. Thus, it has a strict dipolar nature [20]. Another feature which disperses from 9 to 12 eV was recorded in off-specular HREEL spectra. The broadness of its line-shape suggests that it should be assigned to the continuum of the electron-hole pair excitations. In fact, this mode has been demonstrated to be dispersive [46-48].

Hence, the s-like SP and the MP overlap in a broad range in energy–momentum space with the electron–hole continuum. Accordingly, a competition in the excitation between the incoherent electron–hole excitations and the coherent plasmonic modes is expected. However, the overall weight of the electron-hole continuum is higher than that of the collective excitations and this explains the sudden disappearance of the collective mode in off-specular spectra (bottom panel of Figure 1).

Finally, it is worth studying the formation of AuCu alloy. In fact, while many experimental studies have been performed on Au alloying with copper substrates [49-51], collective electronic excitations of the Au-Cu alloy have not been investigated yet. The formation of an Au-Cu alloy upon annealing at 450 K was demonstrated by AES measurements (Figure 3).

As a matter of fact, both Cu and Au contributions are present in the AES spectrum. No trace of alloying was revealed at room temperature, in agreement with previous findings [52].

As regards the electronic spectrum (Figure 4a), the Au SP, recorded at 2.61 eV in the as-deposited film, decreased in intensity upon alloying. Several other features arose upon the formation of the Au-Cu alloy, as evidenced by the analysis of the difference spectrum (Figure 4b). They are ascribed to interband transitions in the alloy located at about 4 eV with respect to the Fermi level. Moreover, an interband transition at 1 eV was observed in the alloy. It should be noticed that an

excitation at similar frequencies was recorded for the clean Cu(111) surface [53], but it was ascribed to a collective excitation of electrons in Shockley surface states of the bare substrate. It disappeared upon deposition of adsorbates [54], as expected for modes related to surface states [55].

## Conclusions

We have shown that the loss spectrum of Au thin films on Cu(111) presents both single-particle and collective excitations. Different excitation channels are in competition each others if they are in the same frequency range. The analysis of the SP dispersion of a thin Au film revealed that the centroid of the induced charge lies less inside the bulk compared with a thick film. Moreover, a broad peak at about 6 eV was observed and assigned to a collective excitation which has both s-like SP and MP character. Another broad feature dispersing from 9 to 12 eV was assigned to the electron-hole continuum. The Au-Cu alloy was formed upon annealing the Au film at 450 K. The loss spectrum of the Au-Cu alloy is dominated by single-particle transitions.

## About the authors

**Antonio Politano** has obtained the PhD in Physics at the University of Calabria (Italy) in 2008. Now he is a post-doc at Instituto Madrileño de Estudios Avanzados (IMDEA) en Nanociencia in Madrid, currently studying gas-surface interaction with helium atom scattering.

**Gennaro Chiarello** (Associate Professor) is a member of the staff of the SPES group (Electronic Spectroscopies of Surfaces) at the Physics Department-the University of Calabria. Their investigation includes the electronic properties of ultrathin alkali and noble-metal films, the chemical reactivity of bimetallic surfaces and alkali coadsorption systems.

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