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Sputtering-induced modification of the electronic properties of Ag/Cu(111)

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Abstract

High-resolution electron energy loss spectroscopy has been used to study the electronic properties of Ag thin films deposited on Cu(111) and modified by Ar⁺ sputtering. Ion sputtering strongly modifies the loss function in the region of single-particle transition as deduced from the appearance of sputtering-induced spectral features in the valence band. In contrast with unmodified Ag systems, in sputtered films the centroid of the induced charge of the surface plasmon lies in the close nearness of the jellium edge. In these modified Ag films, Landau damping processes are activated beyond a critical energy of 3.83 eV and a threshold wave-vector of 0.2 Å⁻¹. Moreover, we found that plural plasmonic losses arose upon increasing Ar⁺ dose. A comparison with the case of the sputtered Ag(100) surface is presented throughout the paper.

1 Introduction

The modification and patterning of solid surfaces induced by ion sputtering has received a considerable interest in recent years [1-7].

Ion beam erosion has great potential applications since it enables a fast and easy way to create large highly ordered features which have been used as templates for the deposition of thin metal overlayers. It has been demonstrated that these patterns can induce magnetic [8, 9] and optical [10] anisotropies in the deposited films. Moreover, also the chemical reactivity of ion-sputtered surfaces is altered [11, 12]. The angle of incidence of the ions can also be used to select the final surface morphology [13-15].

Hence, the control of pattern formation on solid surfaces and interfaces during ion beam sputtering has reached a considerable level of sophistication and the structural modifications of surfaces [1-7] and films [14] bombarded by ions have been now well characterized.

One of the few missing points in this well-established framework is related with the possible existence of effects induced by the ion-beam flux on the electronic properties of the surface. Our aim is to fill this gap by studying the evolution of single-particle and collective excitations of Ag films upon sputtering.

Silver systems are suitable for such scope due to the presence of an intense surface plasmon (SP) [16-19] which makes sputtered Ag films an interesting material for SP-based applications [20]. In addition, the presence of localized d electrons makes unrealistic the jellium model usually applied for describing dynamic screening of simple metals and thus these studies are particularly important from a fundamental point of view. Recently, the presence of sputtering-induced nanoripples on silver crystals has been found to induce an anisotropic optical reflection [2], monitored by

reflectance anisotropy spectroscopy. The ion bombardment results in a plasmonic feature which exhibit a strength increasing with sputter time. The increased amplitude of the SP peak was related to the significant roughening of the surface. Moreover, a direct relationship between the energy of the SP peak and the ripple periodicity was proposed through the analysis of the optical response.

However, careful studies on the electronic properties of ion-modified silver films are not reported yet and this lack must be fulfilled.

More in general, understanding the electronic response of nanostructured thin and ultra-thin films and, in particular, the dispersion relation of their collective modes could provide further information on the physical and chemical properties at the nanoscale.

Previous work for the Ar^+ -sputtered Ag(100) surface showed a drastic change in the dispersion curve of Ag SP [21]. Upon sputtering, the linear coefficient of the dispersion changed from positive to negative, while the quadratic term increased so as to recover the value of the quadratic term of bulk plasmon.

Herein we report on high-resolution electron energy loss spectroscopy (HREELS) measurements on Ar^+ -sputtered Ag films deposited on Cu(111). We found that ion sputtering drastically changes the electronic properties of Ag thin films. Single-particle transitions appear in the sputtered overlayer and the frequency of the SP red-shifted in sputtered films with respect to the annealed film. Single particle transitions (d-sp interband transition at 3.83 eV) affect the Ag SP by broadening its line shape. Even though the energy of the SP does not depend on fluence, its line-width follows a square-root dependence on fluence. The dispersion curve of the SP has a predominant quadratic term and a critical wave-vector for Landau damping has been found to exist. A comparison with the case of the Ar^+ -modified Ag(100) surface is presented.

2 Experimental

Experiments have been carried out in ultrahigh vacuum (UHV) conditions, with a base pressure of $5 \cdot 10^{-11}$ mbar. The substrate is a single crystal of Cu(111). The surface was cleaned by repeated cycles of ion sputtering and annealing at 800 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. Silver was deposited onto the Cu(111) surface by evaporating from an Ag wire wrapped on a tungsten filament. Well-ordered Ag films could be obtained at very low deposition rates (≈ 0.05 ML/min). The occurrence of the p(1x1)-Ag LEED pattern was used as the calibration point of $\theta_{\text{Ag}} = 1.0$ ML. Similar results were obtained by a calibration procedure using AES. Ag coverage was varied from 10 up to 22 ML.

HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS) with an angular acceptance of $\pm 0.5^\circ$. Loss spectra were acquired with a primary electron beam energy of 40 eV. The incident angle with respect to the sample normal was fixed at 55.0° . The energy resolution of the spectrometer was degraded to 10 meV so as to increase the signal-to-noise ratio of loss peaks. All depositions and measurements were made at room temperature. The sputtering of the Ag film was performed also at room temperature, using Ar^+ ions with an impinging energy of 1 keV and in normal incidence as in these conditions diffusion dominates and the surface achieves a morphology that resembles the crystallographic symmetry of the underlying substrate [12]. The Ar^+ flux was 10^{13} ions $\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$. The fluence (flux $\cdot$ time) was varied by changing the sputtering time at fixed flux. The ion sputtering procedure induces a continuous restructuring of the bombarded surface, including

formation of ripples, as a result of the complicated interplay of material removal, ballistic mixing, and diffusional demixing.

Dispersion of the collective mode, i.e., $E_{\text{loss}}(q_{\parallel})$, was measured by moving the analyzer while keeping the sample and the monochromator in a fixed position. The sample was oriented along the $\bar{\Gamma}-\bar{M}$ direction.

To measure plasmon dispersion, values for the parameters E_p , impinging energy, and θ_i , the incident angle, were chosen so as to obtain the highest signal-to-noise ratio. The primary beam energy used for the dispersion, $E_p=40$ eV, provided, in fact, the best compromise among surface sensitivity, the highest cross-section for mode excitation, and $q_{\parallel}$ resolution.

As

$$\hbar \vec{q}_{\parallel} = \hbar(\vec{k}_i \sin \theta_i - \vec{k}_s \sin \theta_s) \quad (1)$$

the parallel momentum transfer, $q_{\parallel}$ depends on E_p , E_{loss} , θ_i and θ_s according

$$\text{to: } q_{\parallel} = \frac{\sqrt{2mE_p}}{\hbar} (\sin \theta_i - \sqrt{1 - \frac{E_{\text{loss}}}{E_p}} \sin \theta_s) \quad (2)$$

where E_{loss} is the energy loss and θ_s is the electron scattering angle [24].

Accordingly, the integration window in reciprocal space is [24]:

$$\Delta q_{\parallel} \cong \frac{\sqrt{2mE_p}}{\hbar} (\cos \theta_i + \sqrt{1 - \frac{E_{\text{loss}}}{E_p}} \cos \theta_s) \cdot \delta \theta_s \quad (3)$$

where $\delta \theta_s$ is related to the angular acceptance α of the apparatus. For the present experiment the momentum resolution was $0.012 \text{ \AA}^{-1}$.

The values of the SP frequency and of the full-width at half maximum (FWHM) were obtained by subtracting a polynomial background and fitting the resulting spectrum by a Gaussian line-shape.

3 Results and Discussion

3.1 Single-particle transitions

The incident argon ions penetrate into the subsurface region and create a collision cascade and thereby atom displacements inside the substrate lattice. Even at low bombardment energies, ion sputtering is known to create vacancies and vacancies clusters in the near-surface region [25, 26] and to induce the presence of embedded Ar.

Beside structural modifications, ion sputtering induces changes in the electronic structure of the surface, as indicated by the analysis of the HREEL spectrum in the region of single-particle transitions. The spectrum of as-deposited Ag film is characterized by a peak at 0.44 eV (spectrum a of Figure 1). No plasmonic modes are expected at such low frequencies [24, 27-29], thus we assign this feature to a single-particle transition. Furthermore, the dispersionless behavior of this feature with the scattering angle (not shown) indicates clearly its physical nature. In fact, an acousticlike excitation, predicted for Ag(111) [30, 31], would have dispersed with the parallel momentum transfer. Very likely, even if existing, the intensity of such plasmonic mode is vanishing in (111)-oriented Ag films due to the screening by the underlying metal substrate.

Upon irradiating the Ag overlayer with Ar^+ , a broad structure centered around 1 eV arose in the surface loss function (spectrum c). The broadness of its line-shape suggests that it should be assigned to the continuum of the electron-hole pair excitations. Very likely, sputtering induces the appearance of an electronic band located at about 1 eV below the Fermi energy.

This finding well agrees with similar experiments on other surfaces. For example, additional spectral features in the valence band have been recorded in photoemission experiments on bombarded diamond surfaces [26, 32].

The intensity of the broad feature at 1 eV increases with Ar⁺ fluence (spectra b and c) while the amplitude of the peak at 0.44 eV decreases up to become only a shoulder in the upmost spectrum of Figure 1. Hence, the valence band of the as-deposited Ag film is significantly modified by sputtering. The filled states introduced by ion bombardment are usually associated with defects [25]. The introduction of a high density of energy states between the valence band edge and the Fermi level is expected to increase the surface conductivity (see Figure 2 and its discussion). For the sake of truth, changes in surface conductivity induced by ion bombardment to date require further clarification.

3.2 Collective excitations

The Ag SP energy for the as-deposited film was found at 3.80 eV (Figure 2). It shifted down to 3.76 eV upon annealing at 400 K due to the flattening of the adlayer. It should be noticed that the shift of the Ag SP frequency from its free-electron value, i.e. 6.5 eV [33], is related to the existence of a strong transition from the occupied *d*-band and the *sp* conduction band [34]. These transitions yield a positive contribution to the dielectric function, producing a red-shift of the bulk and surface plasma frequencies ω_p and ω_{sp} which obey the conditions $\epsilon_1(\omega)=0$ and $\epsilon_1(\omega)=-1$, where ϵ is the macroscopic dielectric response. These frequencies are below but very close to the interband transition. In annealed film the interband transition is expected to be more intense than on disordered films, thus causing a more positive contribution to the dielectric function. This implies a slightly lower SP energy.

Upon Ar⁺-sputtering the Ag film the SP energy shifted to 3.80 eV (Figure 3). The shift of the frequency of the plasmonic excitation upon sputtering apparently contradicts classic theory for which the SP energy is

determined by the real part of the dielectric function and is thus expected to be independent of surface structure and morphology.

It has been demonstrated that the electron density n_e increases upon Ar^+ sputtering [34] as a result of creating defects that act as donors. The blue-shift of the Ag SP energy by 40 meV with respect to the annealed film could be explained within this framework. The very reduced frequency shift of the SP frequency upon sputtering suggests that ion bombardment does not significantly affect the bulk density of electrons [17, 35]. The efficiency, i.e. the number of introduced donors per incoming Ar atom, was found to be very low (10^{-4}) [34]. On the other hand, the slight shift could be also ascribed to variations in the dielectric function of d-band electrons [17, 35], as a consequence of the sputtering-derived shift of the d-band center (see Figure 8b and its discussion).

Thus, our results suggest that n_e saturates for very low Ar^+ dose and this prevents from the observation of a dependence of SP frequency on fluence (see Figure 4 and its discussion). However, upon a new annealing of the film the SP energy moved again to 3.76 eV. This finding demonstrates that the modifications of the electronic properties upon sputtering and annealing cycles of the adlayer may be finely controlled, so as to tune the electronic response of the metal/metal interface.

Likewise, the inspection of the wide spectrum (Figure 3) reveals that the intensity of spectral features at 8.00 and 16.67 eV are recovered upon the second annealing, while an intense and broad peak at 11.48 eV appears only by annealing the sputtered film. The peak at 8.00 eV has a quite complicated nature, as it was ascribed to a single-particle transition [18, 36, 37], the bulk plasmon [18], the s-like SP [18, 38, 39], and the multipole SP

[39]. For Ag/Ni(111) the intensity of this peak has been demonstrated to be in strict relationship to that of the ordinary SP [40]. Concerning the peaks at 11.48 and 16.67 eV, they could be ascribed to collective excitations of the silver film. On the other hand, the intensity of all other loss peaks except the ordinary SP is vanishing in the sputtered film. In particular, the disappearance of the peak at 8.00 eV could be indicative of its multipolar nature. In fact, multipole SPs are very sensitive to the state of the surface as a consequence of its truly surface character [35].

However, it is worth mentioning that the respective contribution of the s-like SP and the multipole SP could not be separated [39].

Results reported in Figure 3 should be put in relationship with the presence of well-defined Ag 5sp-derived quantum well states (QWS) in Ag/Cu(111) even for rather high film thickness [41-44]. Interestingly, it has been observed that the dispersion of QWS changes by annealing the adlayer [45]. Angle-resolved photoemission experiments demonstrated that Ag QWS on Au(111) have flat in-plane dispersion in a disordered film and a nearly free-electron-like dispersion in an annealed and well-ordered film. Accordingly, the sp density of states of the film may be finely tuned by annealing. Hence, spectral features at 8.00, 11.48, and 16.67 eV should be ascribed to the enhancement of the sp density of states in annealed films. They could be assigned to collective modes of the free-electron gas, which are inhibited in the ion-modified interface.

Figure 4 shows the HREEL spectra recorded for different values of the fluence. The frequency of Ag SP in sputtered films was found not to depend on fluence, as it was recorded at a fixed energy for all bombarded

samples. However, in Ag adlayers sputtered with high fluence also peaks at 7.78 and 11.67 eV appeared in the loss spectrum. They were assigned to the first and second replica of the Ag SP. For the sake of truth, the feature at 7.78 eV could also have components related to the above-discussed peak at 8.00 eV. However, the sharpness of its lineshape suggests that it is just a replica of the SP. In fact, its amplitude follows the Poissonian statistics typical of replicas of SP [46].

Multiple SP features appear because impinging electrons may lose energy towards SP excitation more than once [46, 47]. Hence, plural scattering is more favored in sputtered films compared with the as-deposited film. The behavior of ion-modified Ag films is very similar to that displayed by semiconductors and simple metals, while transition metals and their oxides usually display only a single broad plasmon [48].

Such features were absent in the first spectrum of Figure 4 (low-fluence sputtering), thus suggesting that plural scattering is favored by increased disorder.

3.3 Dispersion of the SP

Sputtering induced remarkable changes in the SP dispersion with respect to the case of the as-deposited film (reported elsewhere [49]).

Loss spectra in the region of the SP as a function of the scattering angle are reported in Figure 5 for 22 ML of Ag. The SP shifted from 3.77 up to 3.97 eV as a function of $q_{\parallel}$ (Figure 6).

The dispersion curve could be fitted by a second-order polynomial

$$A + Bq_{\parallel} + Cq_{\parallel}^2$$

(whose values are reported in Table 1), as for the SP of Ag single-crystal surfaces [24].

The linear term is negative, as in sputtered Ag (100) [21] (Table 1), in contrast with Ag surfaces [24]. An initial negative dispersion has been reported also for Ag samples modified by the adsorption of O [50] and Cl [51]. Likewise, a change in the dispersion curve of the SP of a noble-metal has been revealed for self-assembled monolayers deposited on Au(111) films [52].

Nonetheless, the value of the linear coefficient is still sufficiently higher than the linear coefficient of the SP dispersion curve of alkalis [53, 54], aluminum [55], or alkaline-earth metals [56].

According to the Feibelman's model of SP dispersion [57], the linear term is linked to the position of the centroid of the induced charge associated to the electric field of the SP with respect to the position of the geometric surface plane and to the screening properties of the surface, both of which may be affected by sputtering.

In contrast with all other Ag systems [24, 58-60] in which the centroid of the induced charge is well inside the geometrical surface, in ion-sputtered Ag films it lies in the close vicinity of the jellium edge, but not outside as for simple metals.

It should be noticed that the linear term of the dispersion curve is more negative on sputtered Ag(100) (Table 1). However, quadratic terms dominate on both sputtered Ag films and surfaces.

Contrary to the sputtered Ag(100) surface [21] for the quadratic term the bulk value of $6 \text{ eV} \cdot \text{\AA}^2$ [61] was not recovered. In our opinion, the link proposed in ref. 21 between the value of the quadratic term of the SP dispersion and that of the bulk plasmon, related to bulk properties, should be revised.

On the other hand, according to results on Ag SP dispersion reported by Liebsch and coworkers [62-65], 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 in Ag systems [24, 58-60] should be due to the stronger influence of the polarizable medium when the penetration depth of the SP is larger. In modified Ag systems (Ref. 21, 50, and 51 and present measurements) the negative linear term should be put in relationship with a reduced influence of d electrons on SP dispersion.

Important information about the nature of the plasmonic excitation could be provided by the analysis of the backscattering yield as a function of the parallel momentum transfer at frequencies around the SP peak.

The intensity of the SP in the sputtered Ag film as a function of $q_{\parallel}$ has a maximum at $0.20 \text{ \AA}^{-1}$, while the amplitude of the SP in the sputtered Ag(100) surface has a maximum for about $0.10 \text{ \AA}^{-1}$ (Figure 7). Interestingly, the minimum intensity for the sputtered film was recorded for small wave-vectors as expected for dipole scattering [40, 66, 67]. On the other hand, the amplitude of the SP in sputtered Ag(100) has just the opposite trend, i.e. an enhanced intensity was recorded at small values of $q_{\parallel}$, thus suggesting the importance of impact scattering in its excitation.

3.4 Damping of the SP

The lifetime of the SP is a key parameter for understanding collective electronic excitations at metal surfaces and interfaces. It has been demonstrated to strongly influence SP-mediated processes and, moreover, the field enhancement and the sensitivity of surface-enhanced Raman spectroscopy (SERS) [68] and surface-enhanced fluorescence [69].

Hence, studying the decay of the SP excitation into electron-hole (e-h) pairs (Landau damping) through the analysis of the FWHM of the SP peak is essential for understanding SP dynamics.

Long-wavelength SPs are expected to be infinitely long-lived excitations [71]. At finite wave vectors, however, SPs are damped (even at a jellium surface) by the presence of e-h pair excitations [72]. Generally at real surfaces the SP peak is considerably wider than predicted by jellium calculations, especially at low wave vectors, as a consequence of the occurrence of interband transitions and scattering from defects and phonons.

However, it should be noticed that an accurate evaluation of the line-width of a long-lived excitation such as the Ag SP poses a nontrivial problem to theory [73].

The different distribution of occupied and unoccupied electronic states in the ion-modified film (revealed by photoemission experiments [26, 32] and HREELS measurements reported herein) with respect to the as-deposited overlayer would also imply different damping mechanisms of collective excitations.

The joint analysis of the dependence of the FWHM on Ag SP energy and on $q_{\parallel}$ could in principle shed the light on the damping processes of the plasmonic excitation via single-particle transitions.

We compare in Figure 8a the dispersion of the FWHM of the SP of the as-deposited Ag film (reported in Ref. 21) with that of the sputtered Ag film. While for the as-deposited film the FWHM has an initial negative dispersion, the FWHM of the sputtered Ag film is dispersionless for small momenta. For $q_{\parallel} > 0.2 \text{ \AA}^{-1}$ electrons may be promoted from occupied to unoccupied electronic states so that the corresponding plasmon peak would broaden considerably until decaying into the single-particle

excitation continuum.

The FWHM dispersion of Ag bulk samples is instead positive [74, 75] with the existence of a critical wave-vector, as in the sputtered Ag film.

The behavior of the FHMM of the as-deposited film is well described by a theoretical model recently proposed on plasmon lifetime in free-standing Ag layers [70].

The initially negative behavior was ascribed to the splitting between symmetric and anti-symmetric excitation modes and the enhanced electron-hole pair excitation at small $q_{\parallel}$. Evidently such phenomena are inhibited upon sputtering.

On the contrary, a negative behavior of the FWHM has been obtained also for the sputtered Ag(100) surface (spectra reported in Ref. 21), thus excluding that sputtered surfaces behaves similarly.

The behavior of the FWHM as a function of the SP frequency (Figure 8b) clarifies the underlying physical processes at the basis of the difference between the sputtered Ag film and Ag(100). In the sputtered film, the line-width significantly broadened beyond 3.83 eV, while a negative behavior was found on sputtered Ag(100). This means that the damping of the Ag SP in the sputtered Ag/Cu(111) surface is related to the occurrence of the d-s transition at 3.83 eV. Such transition very likely lies at lower energy in the sputtered Ag(100) surface, as indicated by the enhanced FWHM at the lowest Ag SP frequencies.

We suggest that sputtering can modify the surface d-band through inducing shifts of the band center. The energy position of the d-band center is a good indicator of the chemical reactivity of the surface of a transition metal catalyst [76-79]. The d-band theory predicts that the adsorption energy of the adsorbate depends on the position of the center of mass of the d electrons and d holes (the d-band center). It allows relating even small

changes in the electronic structure (due to alloying, the formation of overlayers of one metal on another metal, chemical poisoning and promotion, etc.) to the chemical and catalytic properties of the surface [79-84]. In general, metals with the d-band center closer to the Fermi level are more chemically active than those with the d-band center further away from the Fermi level. Hence, according to results in Figure 8b the sputtered Ag(100) surface is more reactive with respect to sputtered Ag films on Cu(111). As a matter of fact, the analysis of vibrational and AES spectra (not shown) revealed the total absence of contamination in Ar⁺-bombarded Ag/Cu(111) even after several hours after sample preparation.

In view of potential applications, an important requirement is related to sample stability and its chemical inertness, so as obtained for ion-sputtered Ag films on Cu(111).

The line-width of the SP peak increased with fluence (Figure 9, right panel). Moreover, the line-shape of the SP changed upon sputtering. The SP peak became progressively asymmetric, as indicated by the increase of the skewness [85], i.e. the third standardized momentum [86-88], from 0.74 (as-deposited film) to 1.23 (last spectrum of Figure 8) upon sputtering.

The increase of the FWHM upon sputtering is a fingerprint the onset of inelastic processes which shorten the SP lifetime. Very likely, they are caused by the enhancement of Landau damping processes via “phase-breaking” scattering events. Thus, collisions of electrons with lattice defects in the sputtering-modified film are responsible for the progressive broadening of the SP line-width. On the other hand, disorder (induced by the sputtering procedure) has been demonstrated to broaden the imaginary part of the dielectric constant [89], as a consequence of changes in the conduction band which provide additional decay channels, so as to suggest that also modifications in the electronic structure should be taken into account. The continuous modification of the low-energy region of the

HREEL spectrum of Ag/Cu(111) (Figure 1) as a function of the fluence of the sputtering procedure is a fingerprint of the sputtering-induced changes of the electronic structure of the film. The relationship between low-energy single-particle transitions and SP damping processes in Ag thin films has been put in evidence in several previous papers [59, 70, 90, 91].

It is worth mentioning that ion bombardment of a thin film was found to produce both bombardment-induced segregation normal to the film surface and an advancing nanoscale subsurface diffusion zone [92]. Also such physical phenomena should be considered as they are expected to influence SP lifetime.

Figure 10 shows the behavior of the FWHM as a function of the fluence. The FWHM is characterized by a power-law dependence on the fluence (F):

$$\text{FWHM} = \Delta_0 + A \cdot F^{\text{pow}}$$

where $\Delta_0 = (164 \pm 3) \text{ meV}$; $A = (8 \pm 2) \text{ meV} \cdot \text{cm}$, and $\text{pow} = 0.50 \pm 0.06$.

Interestingly, a square-root dependence exists between the FWHM and the fluence F. Accordingly, by varying the fluence it is possible in principle to obtain any desired value of the FWHM, i.e. the SP lifetime. Such finding could influence many phenomena in which SP lifetime plays a pivotal role, such as relaxation processes [93] and the propagation of SP polariton in SP sub-wavelength optics [94]. Moreover, SP lifetime affects the functioning of “superlenses” [95].

The intrinsic lifetime of the SP excitation is proportional to the imaginary part of the dielectric function. The use of plasmonic nanoparticles, such as nanorods or nanoshells, and tuning the plasmon resonance to a wavelength longer than the onset for interband transitions lead to the tunability of the intrinsic damping [96]. This is a consequence of the advanced knowledge today obtained for Landau damping processes in nanoparticles [97] and bulk [98] samples.

Unfortunately, up to now the lifetime of the SP could not be tuned in nanoscale thin films and in general only a few studies exist on SP broadening in thin films [70, 90].

Results reported in Fig. 9 and 10 could constitute a significant advancement also for SP polariton-based applications such as chemical and biological sensors, waveguides, photonic circuits, molecular rulers, optical tweezers [99] and all-optical switching devices [100]. However, it should be noticed that the momentum domain probed by the EELS technique [24, 52, 59, 101, 102] is beyond the momentum range of the SP polariton [94, 103-105], i.e. the long-wavelength limit.

4 Conclusions

HREEL measurements showed that sputtering may be used to create new electronic states in the valence band of Ag films. Plural scattering dominates the electronic response of Ag films sputtered with high Ar^+ dose. The predominant term in the SP dispersion is the quadratic, while the linear is slightly negative. This suggests that the centroid of the induced charge lies in the close vicinities of the jellium edge. The SP peak is significantly broadened by the occurrence of the d-sp interband transition at 3.83 eV, with a critical wave-vector of $0.2 \text{ \AA}^{-1}$.

The lifetime of the SP can be tuned upon sputtering as the FWHM follows a square-root dependence on fluence. On the other hand, the SP frequency is blue-shifted in sputtered films compared with as-deposited Ag layers, but SP frequency is not fluence-dependent.

Such findings could be used for tailoring SP-based devices and claim for theoretical investigations and for angle-resolved photoemission

spectroscopy measurements shedding light on the effects of ion sputtering on the electronic structure of the as-deposited film.

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Figure Captions

Figure 1: HREEL spectra for: (a) as-deposited 10 ML Ag/Cu(111) and the same surface modified by Ar⁺ sputtering with a fluence of : (b) $8 \cdot 10^{16} \text{ cm}^{-2}$ and (c) $14 \cdot 10^{16} \text{ cm}^{-2}$. All spectra were recorded in specular geometry.

Figure 2: HREEL spectrum for the as-deposited Ag film (22 ML) and its modifications upon an annealing at 400 K, Ar⁺ sputtering at room temperature and a further annealing. All spectra were acquired in specular geometry.

Figure 3: HREEL spectrum extended up to a loss energy of 22 eV for the annealed film at 400 K and its modifications upon sputtering at room temperature and a further annealing at 400 K. All spectra were recorded in specular scattering conditions.

Figure 4: HREEL spectrum for 10 ML Ag/Cu(111) as a function of the fluence of the Ar⁺ beam. All spectra were recorded in specular geometry.

Figure 5: HREEL spectra for the sputtered 22 ML Ag/Cu(111) surface as a function of the parallel momentum transfer $q_{\parallel}$, calculated using Eq. 2, and changed by varying the scattering angle at fixed incident angle (55°).

Figure 6: SP dispersion relation for the sputtered 22 ML Ag/Cu(111) interface (our data) and the sputtered Ag(100) surface (data from Ref. 21)

Figure 7: Behavior of the intensity of the SP for the sputtered Ag(100) surface (filled squares, data from Ref. 21) and the sputtered Ag/Cu(111) film (22 ML, empty circles).

Figure 8: Behavior of the FWHM of the SP for as-deposited 22 ML Ag/Cu(111), the same system modified by the sputtering procedure and the sputtered Ag(100) surface (data from Ref. 21).

Figure 9: (left panel) HREEL spectra for 10 layers of Ag/Cu(111). The SP energy shifted from 3.79 eV (as-deposited film) to 3.89 eV, regardless of fluence. On the other hand, the FWHM of the SP peak broadened upon sputtering; (right panel) HREEL spectra after the subtraction of a polynomial background, presented in a restricted energy range. The arrows indicate the value of the FWHM, which increased from 164 to 235 meV upon increasing the fluence.

Figure 10: Behavior of the FWHM as a function of the fluence of the Ar⁺ ion beam.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

	A (eV)	B (eV·Å)	C (eV·Å ²)
Sput. Ag(100)	3.73	-0.98	7.30
Sput. Ag /Cu(111)	3.76	-0.08	2.50

Table 1: SP energy and dispersion coefficients for the sputtered Ag(100) surface (data from ref. 21) and for the sputtered Ag/Cu(111) film (our data, 22 ML).