Probing collective electronic excitations in as-deposited and modified Ag thin films grown on Cu(111)

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The nature and the dispersion of the electronic collective excitations in ultrathin Ag layers deposited onto the Cu(111) surface were investigated by angle-resolved high-resolution electron-energy-loss spectroscopy. For two Ag layers we found a nearly flat behavior of the surface-plasmon energy (absence of dispersion) as a function of the parallel momentum transfer. For higher coverages the surface plasmon is confined in Ag grains. The confinement of the surface plasmon was removed upon annealing. On the contrary, on the sputtered Ag film the quadratic term dominates.

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I. INTRODUCTION

Collective electronic excitations in nanoscale systems have been widely studied in recent years.[1–7] In particular, the behavior of the surface-plasmon (SP) dispersion in ultrathin films deposited on metal and semiconductor surfaces has been the subject of several theoretical[1,7–9] and experimental[3–5,10,11] investigations. Ultrathin films usually exhibit physical and chemical properties markedly different from their bulk counterpart as quantum size effects and electron quantum confinement may occur.[12,13]

In silver samples, considering its *s*-electron density, the energy of the SP is expected to be 6.50 eV, but due to the interaction between *s* and *d* electrons it is lowered to 3.70 eV. Moreover, contrary to alkali-metal systems,[1,4,10,11] the dispersion of Ag SP was found to be positive.[1,2,14–16] A negative dispersion on Ag systems was reported only for modified Ag single-crystal surfaces, i.e., Cl/Ag(111),[17] O/Ag(100),[18] and the sputtered and nanostructured Ag(100).[19] While Ag semi-infinite media have been extensively investigated,[2,14–16] very few experimental studies on low-dimensional Ag systems, such as ultrathin films on metal[5] and semiconductor substrates,[20–22] nanowires,[23] nanoparticles,[24,25] and quantum dots exist. The excitation spectra of Ag films deposited onto an aluminum substrate were calculated by Liebsch[1] using the *s*-*d* polarization model. As expected, the nature and dispersion of the collective excitations calculated for two layers deviated substantially from those reported for multilayers.[5] However, to the best of our knowledge, no experimental study for Ag/metal interfaces supporting such theoretical findings[1] exists. On the other hand, experiments carried out on ultrathin Ag films grown on Si(111) (Refs. 21 and 22) reported a positive behavior of the SP dispersion and, moreover, the collective excitation observed at small momenta was assigned to the ordinary SP. These findings are in contrast with theoretical expectations[1] performed for Ag/Al, thus indicating the existence of strong differences in the electronic response between Ag layers deposited onto metallic and semiconductor substrates. Hence, further experimental work aimed at investigating the nature of the collective excitations in metal/metal interfaces is needed. Such study should provide a significant advancement in understanding dynamic screening processes in the limit of ultrathin metallic layers.

On the other hand, recently, the dispersion of quantum well states (QWS) has been found to change by annealing the adlayer.[26] Angle-resolved photoemission experiments showed 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. Moreover, the possibility of nanostructuring surfaces by ion bombardment was demonstrated by scanning-tunneling microscopy.[27,28] The surface morphology is determined by the interplay between the sputtering and the surface diffusion. Ion-induced nanostructures were observed on Ag(110),[28] Cu(110),[29,30] and Ag(100).[27] The angle of incidence of the ions can also be used to select the final surface morphology.[31] For sputtering at normal incidence, diffusion dominates and the surface morphology resembles the crystallographic symmetry of the underlying substrate: ripples form on Ag(110) and Cu(110) and a checkerboard structure of pits and hills form on Ag(100). The application of ion-sputtering techniques in producing novel nanoscale structures may be of great interest for future applications.[32]

Further information on the physical and chemical properties of such manipulated nanostructured films can be obtained from their electronic excitations and, in particular, from the dispersion relation of the collective modes. A drastic change in the dispersion curve of Ag SP was reported[19] for a sputtered Ag(100) surface. 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 (BP). However, dynamic screening properties of annealed and sputtered Ag films have not been investigated yet.

Herein we present high-resolution electron energy loss spectroscopy (HREELS) measurements shedding light on the nature and the dispersion of the collective excitations in ultrathin Ag layers on Cu(111). This system represents an example of film growth in large (13%) mismatched materials. As the surface energy of Ag and the stress energy at the interface are lower than the Cu surface energy, the Ag ultrathin films grow layer by layer up to two layers.[33,34] Further increasing Ag coverage, three-dimensional Ag islands are formed. Scanning tunneling microscopy and low-energy electron diffraction (LEED) measurements showed that the Ag bilayer form a (9×9) reconstruction.[33,34] Moreover, it is worth mentioning that photoemission measurements of Ag/Cu(111) (Refs. 35–38) revealed the existence of well-defined Ag 5*sp*-derived QWS even for rather high film thickness. This implies the occurrence of an enhanced *sp* density of states at the Fermi level that modifies the electron charge-density distribution. Thus significant changes in the dynamical screening properties[39] with respect to the case of single-crystal surfaces are expected. Hybridization between Ag QWS and the substrate[40] may also influence the electronic response of the interface, and it should be enhanced for very reduced thicknesses, i.e., 2 ML.

Loss measurements reported here demonstrated that in two Ag layers the excitation of SP is not allowed at small momenta. The excitation at $q_{\parallel}\sim0$ is assigned to the ordinary BP. Moreover, for $q_{\parallel}>0.087$ Å^{-1} the SP energy did not exhibit a positive dispersion. Such finding demonstrated that excellent agreement with theoretical calculations performed for two layers of Ag on Al (Ref. 1) exists. Further increasing Ag coverage, the SP is confined within Ag grains. Annealing removed SP confinement and, moreover, induced the occurrence of a negative value of the linear coefficient of the SP dispersion, as a consequence of the enhanced free-electron character of Ag QWS upon annealing.[26] For the sputtered film, the quadratic term of the dispersion was found to be predominant.

II. EXPERIMENTAL

Experiments have been carried out in ultrahigh vacuum (at a base pressure of 5×10^{-9} Pa) on a Cu single crystal cut within 0.1° along the (111) direction. The sample is a 9 mm diameter disk, which was delivered from MaTecK GmbH. It was cleaned by cycles of 1.5 keV sputtering with Ar ions followed by annealing for 30 min to 800–900 K. The structure of the Ag adlayer was analyzed by LEED measurements, showing the characteristic[33,34] diffraction pattern of the reconstructed (9×9) structure in correspondence to the adsorption of the flat bilayer. Ag was evaporated from a heated wire, while the crystal was kept at room temperature. The amount of evaporated Ag was calibrated with Auger electron spectroscopy (AES) and LEED measurements. The energy loss spectra were recorded with an Ibach-type spectrometer at a crystal temperature of 300 K. For the present experiment the momentum resolution was 0.012 Å^{-1}, while the energy resolution was tuned to 10 meV to improve the signal-to-noise ratio of the losses.

III. RESULTS AND DISCUSSION

A. As-deposited Ag thin films

In the case of simple metals it has been demonstrated that the nature of collective electronic excitations occurring in two layers is very different from that in multilayers. For alkali bilayers, the jellium model predicts that at small momenta the SP has a vanishing weight[1,7] and in this limit only BP and multipole plasmon exist.[1] Increasing the coverage above two layers, the excitation of SP becomes possible also in the long-wavelength limit (small momenta).

It would be extremely useful to study dynamic screening processes in the case of Ag bilayers deposited on metallic substrates. In fact, two layers are commonly accepted as a borderline between interface physics and thin-film physics.[1,10,11] Such coverage constitutes the minimal thickness necessary to observe in loss spectra well-distinct features assignable to collective excitations, while the very broad loss features observed from 0 to 2 ML are assigned to single-particle transitions.[11] Increasing the coverage, the nature and the dispersion of the collective excitations in the Ag thin film approach those of bulk Ag.

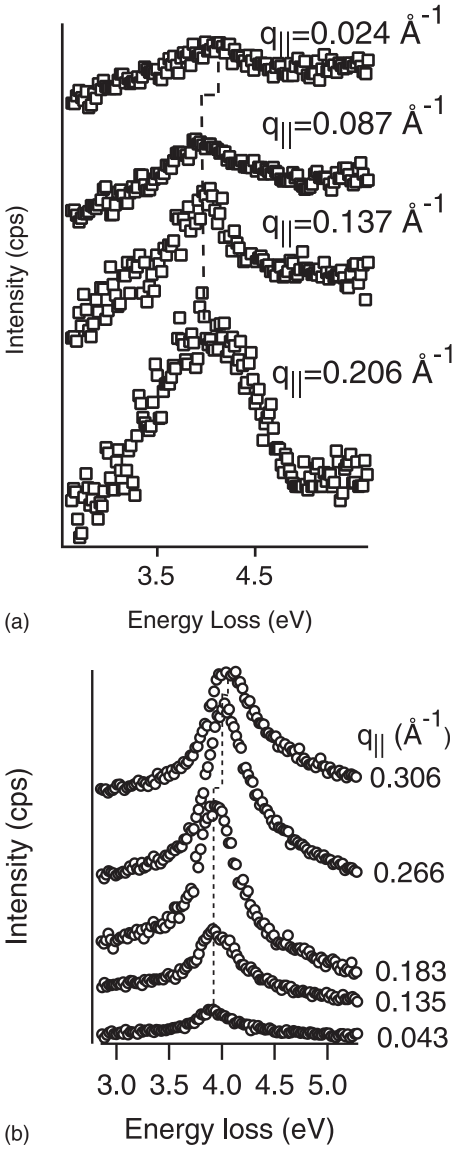

FIG. 1. Selected HREEL spectra as a function of the parallel momentum transfer for 2 ML Ag/Cu(111) (top panel) and 5 ML Ag/Cu(111) (bottom panel) at $T=300$ K.

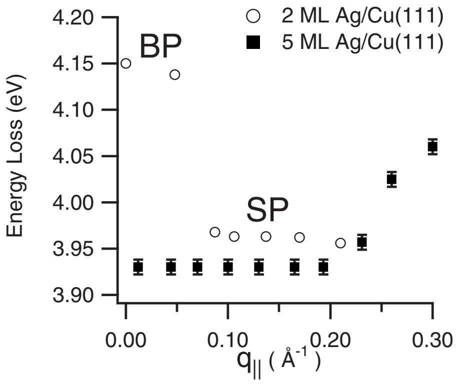

FIG. 2. SP dispersion relation for 2 and 5 ML of Ag on Cu(111) at $T=300$ K.

Selected high-resolution electron-energy-loss (HREEL) spectra for two of Ag/Cu(111) as a function of the parallel momentum transfer are shown in Fig. 1(a) while the energy of the loss features as a function of the parallel momentum transfer is shown in Fig. 2. To obtain the energies of loss peaks plotted in Fig. 2, a polynomial background was subtracted from each spectrum. The resulting spectra were fitted by a Gaussian line shape (not shown).

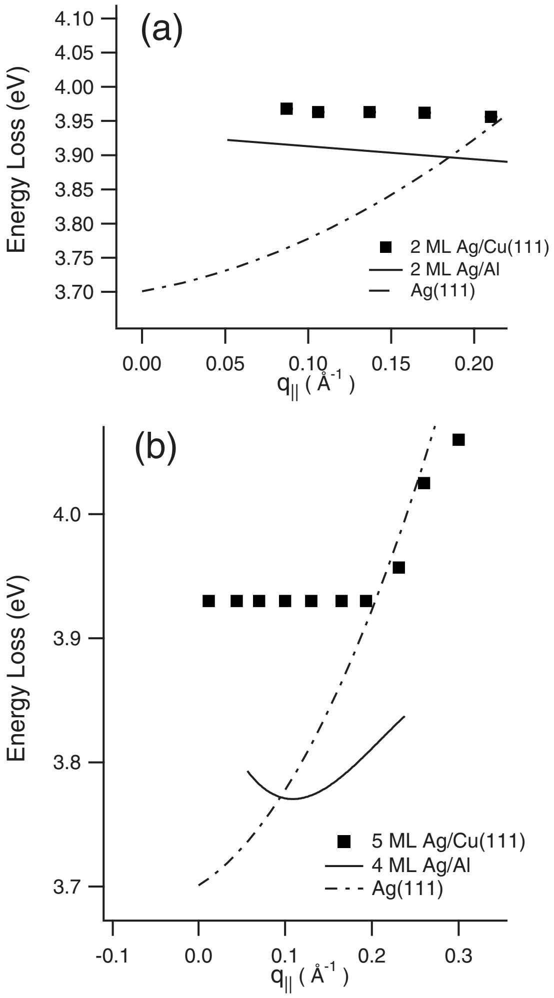

FIG. 3. (a) Behavior of the dispersion curve of the Ag SP for 2 ML Ag/Cu(111) (our data, filled squares), 2 ML Ag/Al (theory, continuous line) (Ref. 1), and Ag(111) (dashed-dotted line) (Ref. 16). (b) Behavior of the dispersion curve of the Ag SP for 5 ML Ag/Cu(111) (our data, filled squares), 4 ML Ag/Al (theory, continuous line) (Ref. 1), and Ag(111) (dashed-dotted line) (Ref. 16).

From Fig. 1(a) it can be observed that at the smallest momenta a loss peak with a very reduced intensity was revealed at about 4.15 eV. The intensity of the loss peak increased notably with $q_{\parallel}$ while its energy underwent a sudden redshift down to 3.96 eV. For $q_{\parallel} > 0.087$ Å^{-1}, the energy of the latter loss peak remained almost constant. We assign the feature at about 4.15 eV to the BP in two Ag layers. On the other hand, the dispersionless feature at 3.96 eV is assigned to the SP in two Ag layers. The significant energy step existing between small and high momenta is due to the different nature of the excitation, i.e., BP and SP, respectively, and not to a rapid change in the SP dispersion. On the other hand, the existence of two well-distinct plasmonic excitations for extremely reduced thicknesses well agrees with the current theoretical picture of collective electronic excitations in thin films.[1,8,9] Both features are strongly blueshifted by *s*-*d* screening[1] compared to their respective values in Ag semi-infinite media, i.e., 3.80 and 3.70 eV, respectively. The blueshift of the SP frequency was previously observed in thin Ag films on Si(111) (Refs. 20–22) and Ni(111),[5] and it is fully described within the framework of the *s*-*d* polarization model.[1] As the thickness of the Ag film is reduced, the overall screening of the charge associated with the SP via the polarizable *d* electronic medium diminishes, giving higher plasmon energy.[1] As regards the blueshift of the BP, it is shifted by *s*-*d* screening at a frequency $\omega_p{*} = \omega_p / \varepsilon_d$, where ε_d is the local dielectric function and ω_p is the *s*-*p* BP frequency.[1] The real part of the dielectric function decreases as the film thickness is reduced, as a direct consequence of the occurrence of a less sharp onset of transitions involving *d* states in thin films compared to bulk Ag.[1] The lack of the SP excitation at $q_{\parallel}=0$ was reported also for ultrathin alkali layers, by both theoreticians[1] and experimentalists.[3] In this case, the surface response function in the long-wavelength limit (small momenta) is peaked at the BP frequency as the overlayer SP has a vanishing weight.[1] On the contrary, in ultrathin and flat Ag layers on Si(111),[21] the SP was excited even at small momenta. Such evidence should be taken as a fingerprint of very different screening processes between 2.5 ML Ag/Si and 2 ML Ag/Cu. The SP was excited at $q_{\parallel} \approx 0$ also for Ag layers on Si(111) nanostructured in islands.[20] However, increasing Ag coverage, i.e., 5 ML [Figs. 1(b) and 2], the SP was excited also at small values of $q_{\parallel}$, as generally found for thick alkali layers.[43] This result suggests that no substantial differences in the electronic response between Ag/Cu and Ag/Si exist for a sufficiently high thickness, so as to reduce the influence of the underlying substrate. As regards the SP dispersion for 2 ML Ag/Cu(111) ($q_{\parallel} > 0.087$ Å^{-1}), it was not positive (Fig. 2), in contrast with all previous measurements on unmodified Ag surfaces[2,14–16] and Ag/Si(111),[21] exhibiting, instead, a positive and quadratic dispersion. In Fig. 3 we compare the SP dispersions for different Ag systems. We notice that strong differences in both energy and dispersion behavior exist for the different cases. Interestingly, the results of present measurements for 2 ML well agree in dispersion with the theoretically predicted behavior[1] [Fig. 3(a)].

Increasing the Ag thickness beyond the bilayer, the Ag film becomes granular.[35–38] Spectra for 5 ML are shown in Fig. 1(b). The analysis of the dispersion relation (Fig. 2) reveals that SP is confined within Ag grains, as indicated by the absence of dispersion below a critical wave vector,[20] i.e., 0.18 Å^{-1}. While the lower energy of the SP has to be ascribed to the increased thickness,[21] the changes in growth mode are responsible for the dissimilarities in the SP dispersion relation. The propagation of the SP can occur only for modes whose wavelength is smaller than the diameter of the single grain. Interestingly, the Ag grains behave like isolated clusters with respect to the plasmonic excitation. The behavior of the SP well agrees with the Stranski-Krastanov growth mode of this system. The increasing strain caused by adsorbed layers destabilizes the film and induces clustering.[41] This behavior arises from the large lattice mismatch between Ag and Cu (13%). It is worth noticing that we have no evidence for the existence of Mie plasmons within Ag islands. Two well-distinct Mie plasmons at 3.1 and 3.9 eV were revealed only for Ag deposited on metal-oxide surfaces[24,25] and not for three-dimensional islands on Si(111).[20] As concerns metal/metal interfaces, the occurrence of Mie plasmons was invoked only for Na quantum dots on Cu(111) (Refs. 12 and 42) but only for a very restricted alkali thickness range. Mie plasmon merged into the ordinary SP already for two nominal Na layers.

It should be noted that in the theoretical investigation for 4 ML Ag/Al,[1] the SP was excited only for momenta higher than 0.05 Å^{-1}. On the other hand for experimental studies on 5 ML Ag deposited on Si(111),[20–22] Ni(111),[5] and Cu(111) (present measurements), the SP was excited even at the smallest momenta, thus suggesting that the thickness dependence of the behavior of the SP dispersion is not appropriately described by *s*-*d* polarization model[1] [Fig. 3(b)].

Important information on collective electronic excitations at metal surfaces could be provided by the dispersion relation of the full-width at half maximum (FWHM). An initial negative behavior of the FWHM was found for both 2 and 5 ML Ag/Cu(111) (Fig. 4), but beyond a critical wave vector the dispersion became positive. This is well described within the framework of a recently proposed[7] theoretical model on plasmon lifetime in free-standing Ag layers. The initial negative behavior was ascribed[7] to the splitting between symmetric and antisymmetric excitation modes. The increased value of the FWHM for 2 ML compared with 5 ML suggests that damping processes of the SP through indirect 5*sp*-5*sp* transition between Ag 5*sp*-derived QWS confined in the adlayer are more efficient for thinner films.

B. Effects of annealing and sputtering on the collective excitations of 22 ML Ag/Cu(111)

The confinement of the surface plasmon in the as-deposited film was revealed also for higher thicknesses, i.e., 22 ML (Fig. 5). In order to remove SP confinement, an annealing of the film at 400 K was performed. Loss spectra in Fig. 7 provided evidence for drastic morphological changes in the film that may be ascribed to a reordering of the film. LEED measurements indicated that a flattening of the Ag adlayer has occurred without the formation of an AgCu alloy (also confirmed by AES).

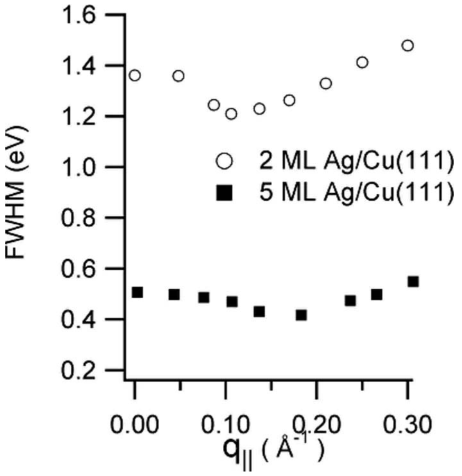

FIG. 4. Behavior of the FWHM for plasmonic excitations on 2 and 5 ML of Ag/Cu(111).

The dispersion curve changed significantly upon annealing and, moreover, the SP confinement was lost. The measured dispersion curve $E_{\text{loss}}(q_{\|})$ of the annealed film, reported in Fig. 6, was fitted by a second-order polynomial given by

$$E_{\text{loss}}(q_{\|}) = A + Bq_{\|} + Cq_{\|}^2,$$

$$A = 3.791 \pm 0.006 \text{ eV}, \quad B = -0.60 \pm 0.09 \text{ eV Å}, \text{ and}$$
$$C = 3.4 \pm 0.3 \text{ eV Å}^2.$$

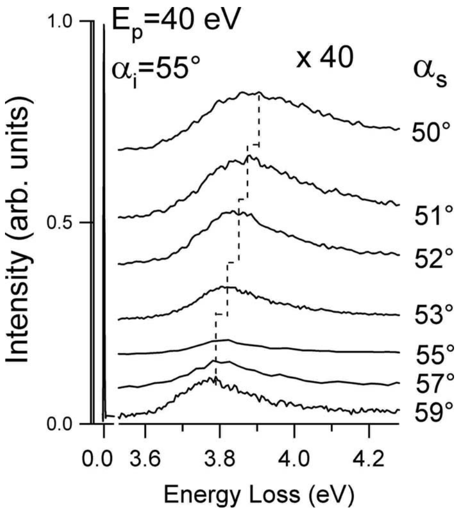

FIG. 5. HREEL spectra for as-deposited 22 ML Ag/Cu(111). All spectra were normalized to the intensity of the elastic peak and multiplied by the same factor. It should be noted that the normalized intensity of the surface plasmon is higher for off-specular spectra, as expected for not purely dipolar excitations.

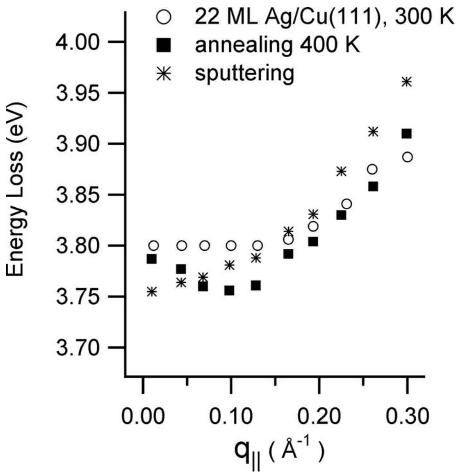

FIG. 6. SP dispersion for as-deposited, annealed, and sputtered Ag films (22 ML) on Cu(111).

The linear coefficient was found to be slightly negative. Recently, it has been found to be null on layer-by-layer Ag films grown on Ni(111).[5] This finding was ascribed to the enhanced *sp* density of states existing in thin Ag films, as a direct consequence of the presence of QWS. Increasing the free-electron character of the QWS by annealing[26] should imply the occurrence of a negative linear term. Nonetheless, the value of the linear coefficient is still sufficiently higher than the linear coefficient of the SP dispersion curve of alkalis, aluminum, or alkaline-earth metals.[2,43] In contrast with all other Ag systems[2,16,21] in which the centroid of the induced charge is well inside the geometrical surface,[44] in annealed Ag films it lies in the close vicinity of the jellium edge, but not outside as for simple metals. Interestingly, the quadratic coefficient coincides with that of SP dispersion in Ag(111),[16] i.e., the surface with the same crystallographic orientation.

Significant differences exist between spectra acquired for annealed (Fig. 7) and sputtered films (Fig. 8). The dispersion curve measured in a sputtered Ag film and reported in Fig. 6 shows that the quadratic term is predominant:

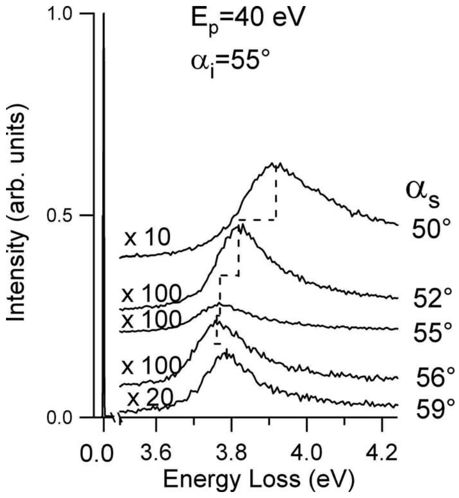

FIG. 7. HREEL spectra for 22 ML Ag/Cu(111) after an annealing at 400 K. Measurements were carried out at 300 K.

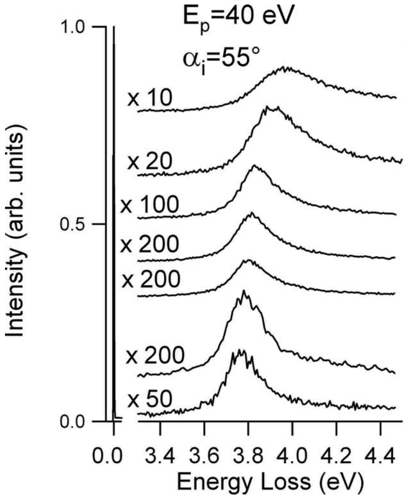

FIG. 8. HREEL spectra for a sputtered 22 ML Ag/Cu(111) surface.

$$A = 3.760 \pm 0.004\ \text{eV},\ B = -0.08 \pm 0.06\ \text{eV Å},\ \text{and}$$
$$C = 2.5 \pm 0.2\ \text{eV Å}^2.$$

Accordingly, an increased linear coefficient and a decreased quadratic term were obtained by fitting procedure. Contrary to the sputtered Ag(100) surface,[19] the bulk value of 6 eV Å^2 (Ref. 45) was not recovered for the quadratic term. Probably, the link proposed in Ref. 19 between the value of the quadratic term of the SP dispersion and that of the bulk plasmon, related to bulk properties, should be revised. The occurrence of an increased linear coefficient suggests that sputtering induces a significant shift of the position of the centroid of the induced charge associated with the SP compared to the case of annealed films. The analysis of the SP dispersion curve seems to exclude the occurrence of SP confinement and, thus, the formation of islands. It is worth mentioning that ion bombardment of a growing film was found to produce both bombardment-induced segregation normal to

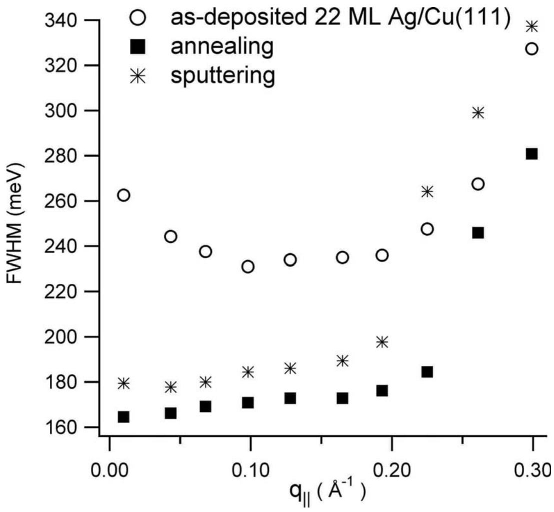

FIG. 9. Behavior of the FWHM for as-deposited, annealed, and sputtered Ag films (22 ML) on Cu(111).

the film surface and an advancing nanoscale subsurface diffusion zone.[46] Both such phenomena should be considered in theoretical studies on the electronic response of sputtered thin films. Moreover, our results provide the grounds for angle-resolved photoemission experiments shedding light on the sputtering-induced modifications of the QWS. Concerning the SP damping, it is worth mentioning that the behavior of the FWHM for single-crystal Ag surfaces is positive[2,16] and was recovered by annealing the Ag film (Fig. 9).

IV. CONCLUSIONS

In conclusion, our results demonstrated that the SP dispersion in an Ag bilayer on Cu(111) is not positive, in contrast with all previous measurements on Ag semi-infinite media. At small momenta, at which the SP has a vanishing weight, the feature observed in loss spectra was assigned to the BP, in agreement with theory and with previous results on alkali ultrathin layers. Significant differences found between 2 ML and higher coverages of Ag/Cu(111) are clear experimental evidence of the changes occurring in screening processes as Ag thickness increases, and also of changes in the growth mode. SP is confined within islands in as-deposited Ag layers on Cu(111) for Ag thicknesses beyond the bilayer. The annealing of the Ag adlayer causes the loss of SP confinement and determines an enhancement of the free-electron density of states, which renders slightly negative the linear coefficient of the dispersion relation. On the other hand, sputtering induces an increase in the linear term and a decrease in the quadratic term.

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