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Surface plasmon dispersion on sputtered and nanostructured Ag(001)

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The surface plasmon dispersion of ion bombarded Ag(001) is investigated by angle resolved high resolution electron energy loss spectroscopy. We find it to be parabolic and dominated by the quadratic term, contrary to the case of flat Ag(001) where the linear term is dominant. The case is reminiscent of surface plasmon dispersion on the oxygen covered, missing row reconstructed Ag(001) surface, for which case the change of the dispersion from nearly linear to quadratic was attributed to the removal of a surface plasmon decay channel associated to the surface interband transition at $\bar{X}$. We show moreover, that for the sputtered surface, slope and curvature of the dispersion depend on surface morphology at the nanoscale. When sputtering is performed at low crystal temperature and no ordered superstructure forms, the quadratic term coincides with the isotropic value dictated by bulk properties, reported for flat Ag(110) and Ag(111) and for reconstructed Ag(001). When on the contrary sputtering is performed at room temperature and the checkerboard superstructure develops, the quadratic term becomes twice as large.

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I. INTRODUCTION

Collective electronic excitations at metal surfaces have been widely investigated as they affect a variety of surface properties ranging from photoemission and chemisorption to surface optics.[1–4] The surface response properties were demonstrated to be linked to the initial dispersion of the surface plasmon, which can be determined by low energy, angle resolved high resolution electron energy loss spectroscopy (HREELS). In particular Ag surfaces became a paradigm for this kind of studies because of the sharpness of the surface plasmon loss, which allowed to investigate the dependence of its dispersion on crystal face,[2] adsorbate coverage,[5] and adsorption induced reconstruction.[6,7] The anisotropy of surface plasmon dispersion with respect to crystal face[2] and its modification induced by Cl adsorption[5] on Ag(111) were ascribed to the different screening of the Ag($4d$) electrons.[5] The change of the dispersion from mainly linear to quadratic, observed upon the onset of the missing row reconstruction on Ag(001) was on the contrary tentatively explained by the removal of a surface interband transition (SIT), whose energy nearly matches the one of the surface plasmon.[6,8] More recently also the size of the grains of an ultrathin Ag film was demonstrated to influence surface plasmon dispersion,[9] because of the localization of the surface plasmon within the grains.

Given the growing interest in nanoscience, investigating more thoroughly the effect of surface disorder and nanostructuring on surface plasmon dispersion becomes an attractive task. In the past, the surface plasmon frequency was studied optically for Ag surfaces obtained by anodic dissolution and subsequent deposition of several atomic layers in cyclic voltammetry,[10] a treatment which causes a roughness of several hundreds of nanometers. A splitting of the surface plasmon resonance[11,12] was observed because of wave vector mixing. More recently the possibility of nanostructuring surfaces by ion bombardment was demonstrated by scanning tunneling microscopy.[13,14] The equilibrium surface morphology is thereby determined by the interplay between the removal action due to sputtering and the healing effect of surface diffusion. For a face centered cubic (001) surface a checkerboard structure of truncated pyramidal pits forms whenever the mobility is large enough, i.e., above a sputtering temperature T_{sput} of 250 K. The roughness, defined as the root mean square deviation of the height distribution, reads typically some 10 Å and the superstructure periodicity is in the range of 60–600 Å, depending on the fluence of the sputtering beam and on crystal temperature.

In the present paper we show how this treatment modifies surface plasmon dispersion, which changes from nearly linear, as appropriate for flat Ag(001),[2] to an almost quadratic shape. The change is observed also when sputtering at low crystal temperature, where no ordered structures form, although the parameters describing the dispersion curve are different in this case.

II. EXPERIMENTAL

The surface plasmon frequency is measured as a function of parallel momentum transfer $q_\parallel$ by angle resolved high resolution electron energy loss spectroscopy. Results for two different sputtering temperatures $T_{\text{sput}} = 105$ K and $T_{\text{sput}} = 300$ K, corresponding to a disordered surface and to the checkerboard superstructure, respectively, are reported.

The HREEL spectrometer is tuned at an electron impact energy $E_e = 15.6$ eV. The transferred momentum is varied by changing the angle of incidence of the electrons, using the same method employed in our laboratory in previous experiments.[6,15] The energy resolution of the incident beam is degraded set to 20 meV in order to achieve a reasonable count ratio. The angular acceptance of the spectrometer is typically 1°, corresponding to integration in reciprocal space over ≈ 0.03 Å^{-1} in our experimental conditions. The wavevector mixing for heavily damaged surfaces may however exceed this value by a factor up to 6.

Before each experiment the Ag(001) surface was cleaned

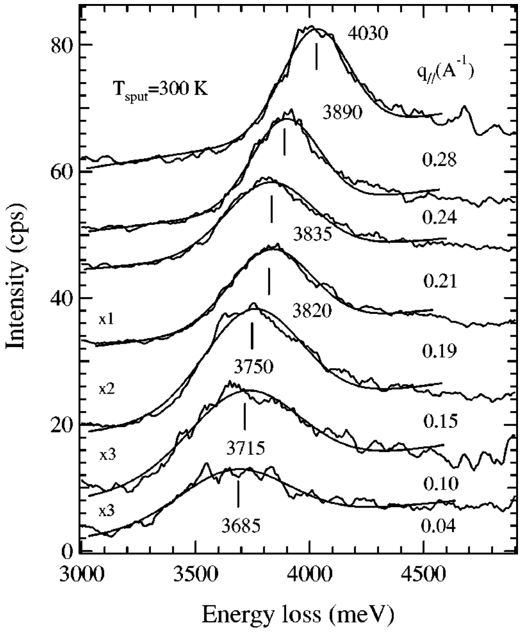

FIG. 1. Sample spectra showing the surface plasmon loss at different $q_\parallel$ for the surface covered by a checkerboard structure obtained by sputtering at $T_{\rm sput}=300$ K. The continuous line is the best fit given by a Gaussian plus a linear background.

by sputtering and annealing cycles to 740 K. The surface is then nanostructured by sputtering at the desired temperature. For the $T_{\rm sput}=300$ K experiments the crystal is then rapidly cooled down to quench surface mobility, reaching temperatures below 150 K within a few minutes. The HREEL spectra are then recorded at $T=105$ K. We worked at a sputtering flux of 10^{13} ions cm^{-2} sec and a fluence of 1.8×10^{15} ions cm^{-2}, which imply that the roughness reads 6 Å when $T_{\rm sput}=300$ K.[14]

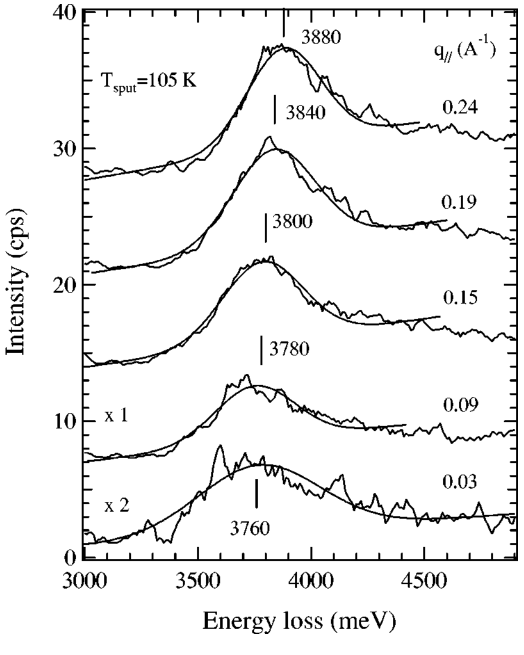

FIG. 2. Sample spectra showing the surface plasmon loss at different $q_\parallel$ for the surface obtained by sputtering at $T_{\rm sput}=105$ K. The continuous line is the best fit given by a Gaussian plus a linear background.

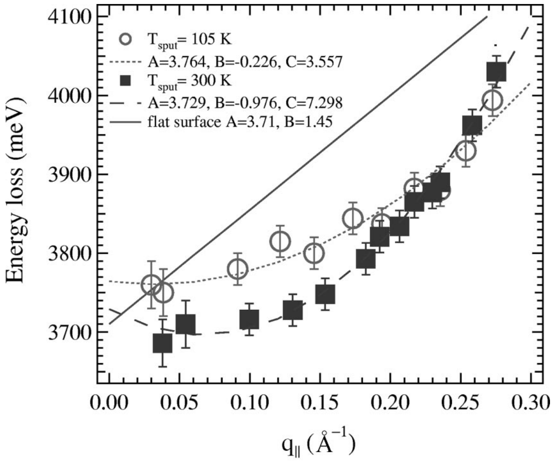

FIG. 3. Surface plasmon dispersion curves as a function of $q_\parallel$ for two different sputtering temperatures (squares: $T_{\rm sput}=300$ K; circles: $T_{\rm sput}=105$ K) and best fit curves. The linear best fit of the dispersion on the flat surface (solid line)[2] is reported, too.

III. DATA PRESENTATION AND ANALYSIS

In Fig. 1 we show HREEL spectra recorded at different $q_\parallel$ for the Ag(001) surface sputtered at $T_{\rm sput}=300$ K. The losses are considerably broadened compared to the flat surface case: the full width at half maximum (FWHM) at $q_\parallel=0.10$ Å^{-1} reads between 400 and 500 meV, against 150 meV measured for flat Ag(001). The position of the maximum of the energy loss peaks $E_{\rm loss}$ is, however, still well defined and can be determined by fitting the experimental points with a gaussian plus a linear background. The loss peak is identified with the surface plasmon excitation.

The twin experiment performed using $T_{\rm sput}=105$ K is reported in Fig. 2. The spectra show peaks of comparable broadness but fainter intensity so that, in spite of the longer acquisition times employed in this case, the data are characterized by a worse signal to noise ratio.

The maximum of the energy loss peaks is plotted in Fig. 3 as a function of $q_\parallel$ for the two different sputtering temperatures. The dotted and dashed curves are the result of a best fit procedure with the parabolic form

$$E_{\rm loss}=A+Bq_\parallel+Cq_\parallel^2. \tag{1}$$

The solid line is the dispersion of the flat surface taken from Refs. 2,15. Compared to the flat surface case the data points of the sputtered surfaces are clearly downshifted at large $q_\parallel$ so that the apparent dispersion curve acquires a definitively non zero quadratic term, while the loss energy at $q_\parallel=0$ is shifted to higher values especially for the coldly sputtered surface. The best fit parameters are reported in Table I (rows with $\Delta\theta=0$).

TABLE I. Parameters of the best fit function $A+Bq_{\parallel}+Cq_{\parallel}^2$, for the dispersion curve of the surface plasmon at $T_{\text{sput}}=105$ and 300 K. $\Delta\theta=0$ means that the data were not deconvoluted with respect to wave vector mixing.

T_{sput} (K)	$\Delta\theta$ (deg.)	A	B	C	χ^2
105	0	3.76	−0.23	3.56	0.90
105	6	3.70	0.23	3.35	0.76
300	0	3.73	−0.98	7.30	0.34
300	1	3.705	−0.56	5.98	0.30

IV. DISCUSSION

Let us first address the shift of $E_{\text{loss}}(q_{\parallel}=0)$. This result is surprising as it apparently contradicts classic theory for which the surface plasmon energy is determined by the bulk dielectric function and is thus expected to be independent of surface structure and morphology. This is indeed the case for all flat low Miller index surfaces of Ag for which the surface plasmon energy reads $\hbar\omega$ 3.70 eV, when determined by energy loss spectroscopy-low energy electron diffraction (ELS-LEED),[16] and 3.71 eV when determined by HREELS experiments.[2] The value of 3.70 eV is probably more accurate as integration in reciprocal space is smaller with ELS-LEED. A small shift was however reported with ELS-LEED for K/Ag(110) (Ref. 17) indicating that classic theory might fail in particular circumstances. For the sputtered, disordered surface the effect is apparently much larger. We shall prove in the following that, in the present case, the shift can be explained by wavevector mixing due to surface roughness.

The true surface plasmon energy at given $q_{\parallel}$ $E_t(q_{\parallel})$ can be recovered by deconvolution with respect to integration in reciprocal space. Let $\sigma(q_{\parallel})$ be the cross section at the corresponding momentum transfer[18] and assuming that the distribution is gaussian with width δ the convoluted maximum of the energy loss is shifted to

$$E_c(q_{\parallel})=\frac{\int e^{-(\xi/\delta)^2}\sigma(q_{\parallel}+\xi)E_t(q_{\parallel}+\xi)d\xi}{\int e^{-(\xi/\delta)^2}d\xi}. \tag{2}$$

δ can be derived from the experimental angular half width at half maximum of the specular peak $\Delta\theta$ which reads 6° for $T_{\text{sput}}=105$ K and is nearly equal to the angular acceptance of the spectrometer $\alpha=1°$ for $T_{\text{sput}}=300$ K. The deconvolution procedure is thus absolutely necessary for $T_{\text{sput}}=105$ K, while it has a smaller effect for $T_{\text{sput}}=300$ K. The best fit curves obtained with Eq. (2) are reported in Figs. 4 and 5 for $T_{\text{sput}}=105$ K and $T_{\text{sput}}=300$ K, respectively. The corresponding parameters are again collected in Table I.

For the surface plasmon frequency $\hbar\omega(q_{\parallel}=0)$ values are recovered, which are compatible with the surface plasmon frequency of the flat surface for both T_{sput}. For the coldly sputtered surface two minima of χ^2 are present: at $\hbar\omega(q_{\parallel}=0)=3.70$ eV and $\hbar\omega(q_{\parallel}=0)=3.75$ eV. Although the χ^2 value is slightly better for the latter value ($\chi^2=0.67$ against 0.76), the difference is too small to justify the assumption that classic dielectric theory is violated. We therefore conclude that no shift of the surface plasmon energy takes place at $q_{\parallel}=0$, also for the coldly sputtered surface.

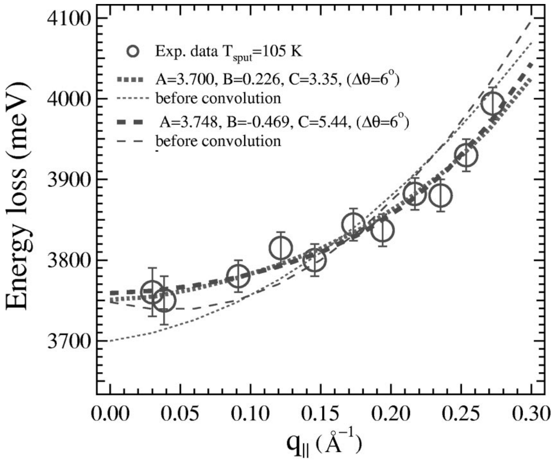

FIG. 4. Surface plasmon dispersion curves for $T_{\text{sput}}=105$ K. The experimental data are reported as a function of $q_{\parallel}$ and compared with the two best fit curves obtained by χ square analysis after deconvolution with respect to roughness induced wavevector mixing. The curves are reported before (thin lines) as well as after (thick lines) the convolution procedure.

Let us address now the modification of the shape of the surface plasmon curve caused by sputtering. As shown in Table I both the decrease of the linear coefficient and the increase of the quadratic term with respect to the flat surface values persist after deconvolution. The linear term is linked both to the position of the centroid of induced charge with respect to the position of the geometric surface plane and to the screening properties of the surface,[5] both of which may be affected by sputtering.

More striking than the change in the linear term is the growth of the quadratic term. For the coldly sputtered surface it reads 3.35 eV Å^2 and is thus compatible with the isotropic value of 3.4 eV Å^2 reported for flat Ag(110) and Ag(111),[16] thus supporting the conclusion that this quantity

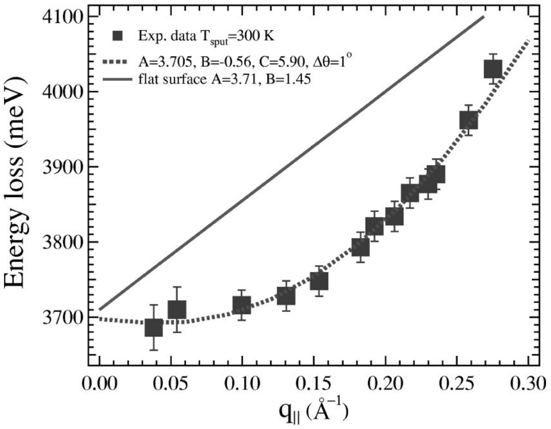

FIG. 5. Surface plasmon dispersion curves for $T_{\text{sput}}=300$ K. The data are reported vs $q_{\parallel}$ and compared with the parabolic best fit curve after the convolution with respect to angular integration.

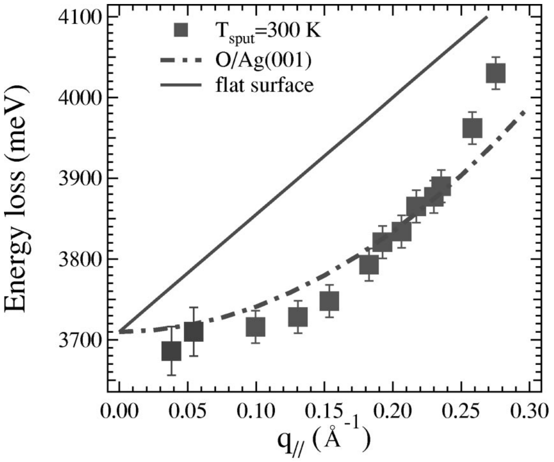

FIG. 6. Comparison of the surface plasmon dispersion measured for the flat surface (continuous line), 0.05 ML oxygen on flat Ag(001) (missing row reconstructed surface, dash-dotted line, taken from Ref. 6) and for the checkerboard reconstructed phase (squares).

is determined by bulk properties and that the bulk value is recovered once the anomaly of Ag(001) is removed.

Following Zacharias and Kliever[19] the bulk plasmon on Ag has a purely quadratic dispersion with the quadratic term given approximately by the expression for a free electron gas

$$B=\frac{3\hbar E_F}{5me\omega_p}=6.3(\text{eV}\,\text{Å}^2), \tag{3}$$

where $\hbar\omega_p$ is the bulk plasmon energy, E_F the Fermi energy, and m and e the effective mass and the charge of the electron, respectively. Although Eq. (3) has no theoretical justification for a noble metal as Ag, the measured value of 6.3 eV Å^2 was shown to come out assuming for the measured value $\hbar\omega_p=3.78$ eV, and m equal to the free electron mass. Alternatively it can be recovered assuming for the plasmon energy the value calculated for a free electron gas with one electron per atom, $\hbar\omega_p=8.4$ eV, and an effective mass of about half the free electron mass, a reasonable value for the band structure of Ag. The isotropic quadratic term of the surface plasmon dispersion (3.4 eV Å^2) differs therefore by a factor 2 from the bulk value, most probably because of the different band structure at the surface. Interestingly for the nanostructured surface the quadratic term reads 5.9 eV Å^2 and coincides thus, within error, with the value determined from bulk plasmon dispersion.

A comparison of the data for the nanostructured surface with the dispersion obtained for the missing row reconstructed system at 0.05 ML oxygen coverage[6] is shown in Fig. 6. Independently of the numerical value of the best fit parameters (reading $A=3.71$ eV, $B=0$, $C=3.1$ eV Å^2 for the oxygen covered surface), whose determination can be affected by compensation effects, it is apparent that the dispersion of the surface plasmon is very similar in the two cases. The removal of the anomaly of Ag(100) takes therefore seemingly place both for the sputtered surface and for the missing row reconstructed surface restoring in both cases a dispersion with a large quadratic term.

The change of the form of the surface plasmon dispersion was suggested to be associated to the elimination of a surface interband transition (SIT) nearly degenerate with the surface plasmon frequency which constitutes therefore an efficient decay channel. This interband transition is at $\overline{X}$ and involves a filled Shockley state present just below the Fermi level E_F and an empty Shockley state at 3.5 eV above E_F.[20,21] A recent photoemission spectroscopy investigation confirmed that the former state is quenched for the reconstructed surface,[8] being shifted above the Fermi level by the reduction of the atomic density at the surface.[22] The decay channel for the surface plasmon is thus eliminated and the quadratic dispersion restored. Similar, reconstruction induced, shifts of the surface states were demonstrated experimentally also for H/Ni(100) (Ref. 23) and for Na/Cu(110).[24] This interpretation is therefore plausible also for our present results as ion bombardment causes a reduction of the atomic density and an, at least a partial, removal of the SIT is expected for both T_{sput}. An investigation of the effect of sputtering on the surface electronic states is, however, not available, so that other mechanisms cannot be excluded *a priori*; a minimal hypothesis is, however, able to rationalize a wide set of experimental observations.

Finally let us comment on the difference of the quadratic term for surfaces with different nanostructures. The effect is beyond the experimental error since (i) the data points coincide at large $q_\parallel$, (ii) the surface plasmon frequency must be the same for vanishing $q_\parallel$, where it is dictated by bulk properties, (iii) at intermediate wave vectors the energy loss observed after sputtering at room temperature is at definitely lower energy. Nanostructuring the surface at the 10 nm scale affects therefore surface plasmon dispersion.

We discuss three possible causes for this phenomenon, none of which is, in our opinion, really satisfactory: (i) occurrence of surface plasmon confinement, (ii) peak shift due to the excitation of surface interband transitions, (iii) true modification of the dispersion shape.

Hypothesis (i) is appealing, but it has to be rejected since surface plasmon confinement would be expected to increase the surface plasmon energy at wavelengths larger than the confinement region, where propagation in inhibited and the surface plasmon behaves as an Einstein oscillator, as reported in Ref. 9 for ultrathin Ag films deposited on Si. Our data show, on the contrary, that the surface plasmon has the expected frequency in the long wavelength limit.

Hypothesis (ii), the excitation of additional electronic excitations either absent or which cannot be excited on flat and on disordered surfaces, cannot be ruled out in principle. Shifts of the loss peak position from the one expected for the surface plasmon were reported for Ag(110) as well as for Ag(111) (Ref. 25) and attributed to the excitation of a multipole plasmon mode, while interband transitions are known to be intense for Ag(110).[2,26] In both cases, however, the shift is to higher energy losses, contrary to the present result.

Hypothesis (iii) lacks of theoretical justification. Nanostructuring the surface could have the effect of recovering the true bulk value of 6 eV Å^2 for the quadratic term. Alternatively one could imagine that nanostructuring introduces a cubic term in the form of the dispersion curve. Indeed if we keep the terms A and C, corresponding to the surface plasmon frequency and to the quadratic term, fixed at the bulk values and allow for a cubic term D in the fitting procedure we obtain $B=-0.24$ eV Å and $D=5.3$ with $\chi^2=0.27$, slightly better than for the purely parabolic fit. This approach has, however, no justification except of preserving the quadratic term at the isotropic value.

V. CONCLUSIONS

In summary we found that for the sputtered surface: (a) the value of the surface plasmon energy $\hbar\omega(q_\parallel=0)$ is unchanged within experimental error with respect to the flat surface case as required by classical theory, (b) the plasmon dispersion becomes parabolic with a strongly reduced first order term and a dominant quadratic term which has the same value as for flat Ag(110) and Ag(111), at least for $T_{\mathrm{sput}}=105$ K, (c) for the nanostructured checkerboard superstructure the parabolic fit yields a larger quadratic term than for the coldly sputtered case.

The present results are in accord with our previous conclusion that the nearly linear dispersion of flat Ag(001) is anomalous[2] and that this anomaly can be eliminated by modifying the surface structure.[6] This takes place effect is present both when the surface is reconstructed by oxygen adsorption or, as demonstrated here, when the surface atom density is reduced by sputtering.

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