ELS-LEED study of the surface plasmon dispersion on Ag surfaces

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Abstract

An energy loss spectroscopy–low energy electron diffraction (ELS–LEED) study of surface plasmon dispersion on Ag(111) and Ag(110) is presented. This new technique allows us to improve the resolution in k-space, which constitutes the major limiting factor for studying surface plasmon dispersion. The uncertainty in the determination of the dispersion coefficients is thus improved by more than a factor of two with respect to conventional HREELS. In accord with previous literature we find for both Ag faces a positive dispersion, which is anisotropic with respect to the crystal face and, for Ag(110), to the crystal azimuth. The quadratic term, on the contrary, is isotropic. © 1997 Elsevier Science B.V.

Keywords: Energy loss spectroscopy; Low energy electron diffraction; Silver

1. Introduction

Surface plasmons and dynamical screening properties at metal surfaces recently attracted considerable attention, as they play a significant role in transport and optical properties of metals [1]. Surface plasmon dispersion is particularly important as it is related, for simple metals, to the position of the centroid of the screening charge at the surface [2,3]. As demonstrated by angle resolved high resolution electron energy loss spectroscopy (HREELS) and in accord with theory [2], the latter quantity is located outside of the geometric surface, as the initial dispersion is negative [3–5].

On the contrary the surface plasmon on Ag surfaces [6–12] showed a positive dispersion which is anisotropic with respect to the crystallographic face and, for Ag(110), also to the crystal azimuth. The origin of such an effect is obviously connected to the presence of d-electrons, but the microscopic mechanism is still debated theoretically and no quantitative results could be achieved for the dispersion anisotropy [13].

The experimental accuracy can now be strongly improved by applying energy loss spectroscopy–low energy electron diffraction (ELS–LEED), the inelastic analog of spot profile analysis of LEED (SPA–LEED), which permits one to improve the resolution in reciprocal space, thus removing one of the major experimental limita-
tions in the study of surface electronic excitations. Such a technique is applied here to the study of surface plasmon dispersion on Ag(111) and Ag(110). The reinvestigation allowed one to show the complex nature of the losses determined by the presence of the multipole plasmon mode [14]. Such a mode is particularly evident near to \( q_{\perp} = 0 \) where the dipole scattering intensity, by which the ordinary surface plasmon is excited, has a minimum.

In this paper we analyse the surface plasmon dispersion and its anisotropy with respect to the crystal face and, for Ag(110), to the crystal azimuth. In accord with previous literature we find that the linear dispersion coefficient is anisotropic, whereas the quadratic term, generally attributed to bulk effects, is isotropic.

2. Experiment

The newly developed ELS–LEED spectrometer [15,16] consists of a single monochromator of 127° cylindrical deflector-type and of an identical analyser, whereas the high \( q_{\perp} \) resolution is achieved thanks to an octupole deflection system. The electrostatic deflection system allows scanning through \( k \)-space without tilting the crystal. The scattering geometry has near normal incidence and detection (specular reflection occurs at \( \theta = 6^\circ \)). Such a system, therefore, allows one to investigate each point of reciprocal space for any preset energy loss. The transfer width of the instrument is 1500 Å, which corresponds to a momentum resolution of \( \Delta q_{\perp} = 0.004 \text{ Å}^{-1} \). \( \Delta q_{\parallel} \) is, however, generally limited by the quality of the crystal, i.e. by its mosaic structure determined by dislocations.

The experiment was performed in ultra high vacuum \( (2 \times 10^{-10} \text{ mbar}) \) on a commercial Ag(111) crystal and on a dislocation-free Ag(110) crystal. The surfaces were prepared in the usual way [1] by ion sputtering and annealing until no traces of impurities could be detected by Auger electron spectroscopy or by ELS–LEED.

From the angular width of the specular peak the resolution in reciprocal space was determined to be \( \Delta q_{\parallel} = 0.038 \text{ Å}^{-1} \) for Ag(111) and \( \Delta q_{\parallel} = 0.021 \text{ Å}^{-1} \) for Ag(110). The latter value is half as large as in previous work and is determined by the dislocations created during surface preparation. The quality of the data for Ag(111) is, however, better than in the case of HREELS measurements on the same crystal [11], because of the electronic control of the scattering geometry. The energy resolution was tuned to 20 meV to improve the signal-to-noise ratio for the losses. The spectra were recorded at a crystal temperature of 90 K.

3. Data presentation

Sample spectra recorded for Ag(110) in the two crystallographic directions \( \langle 100 \rangle \) and \( \langle 110 \rangle \) at different \( q_{\parallel} \) are shown in Fig. 1. As discussed in detail elsewhere [14], for these scattering conditions the peak corresponds to the excitation of the surface plasmon, the contribution of the multipole mode being negligible. The surface plasmon frequency \( \hbar \omega_{\text{sp}} \) can thus be inferred from the position of the maximum of the loss peak, and it is determined, after the subtraction of an inelastic background due to electron–hole pair excitations, by a Gaussian fit. The transferred momentum parallel to the surface \( q_{\parallel} \), is then calculated from the impact energy \( E_i \), from \( \hbar \omega_{\text{sp}} \), and from the scattering geometry applying energy and momentum

![Fig. 1. Energy loss spectra for Ag(110) recorded at \( E_i = 65.4 \text{ eV} \) for the directions (a) \( \langle 100 \rangle \) and (b) \( \langle 110 \rangle \).](image-url)
conservation:

$$q_{ii} = \frac{\sqrt{2mE_{i}}}{\hbar} (\sin \theta_{i} - \sqrt{1 - E_{\text{loss}}/E_{i}} \sin \theta_{s}). \quad (1)$$

As one can see, both the dispersion and the $q_{ii}$ dependence of the peak width are anisotropic with respect to the crystal azimuth, the peaks being shifted to larger frequency and being broader along $\langle 001 \rangle$. Similar data were recorded for other impact energies for Ag(110) and Ag(111).

4. Surface plasmon dispersion

The values of the maximum of the energy loss ($\hbar \omega_{\text{sp}}$) of the peaks are reported vs. $q_{ii}$ in Fig. 2a for Ag(110) along the two high symmetry directions and in Fig. 2b for Ag(111). The inset shows the region near to $q_{ii} = 0$ for Ag(110) to highlight the azimuthal anisotropy of the data. The curves were fitted with a parabolic form:

$$\hbar \omega_{\text{sp}}(q_{ii}) = \hbar \omega_{\text{sp}}(0) + Aq_{ii} + Bq_{ii}^2. \quad (2)$$

The best fit parameters and the uncertainties were determined by the $\chi^2$ method using the MINUIT computing routine. The large uncertainty on $q_{ii}$ was thereby reported on the dependent variable. The quality of the data is such that an error as small as $\pm 2.5 \text{ meV}$ had to be assumed to get unitary statistical variance. The results is shown in Table 1.

As one can see, $h \omega_{\text{sp}}(0)$ agrees within experimental error for the three cases. It is, however, slightly lower than the value determined by HREELS for Ag(001) ($3.710 \text{ eV at } T = 100 \text{ K} \ [17]$) and Ag(111) ($3.708 \text{ eV at } T = 100 \text{ K} \ [11]$). While the reason for the discrepancy is still unclear, we note that our value is in better agreement with the optical value $3.665 \text{ eV}$ according to Ref. [18].

All curves have the same quadratic coefficient, whereas the linear term is different. This confirms the previous results of Rocca et al. [11], that the anisotropy has surface origin. We note that the errors on the coefficient are improved in the present study by a factor two to four. On Ag(111) the linear term on the dispersion is nearly identical with the previous determination, whereas the quadratic term is slightly larger (it reads $2.7 \pm 0.5 \text{ eV } \text{Å}^2$ in Ref. [11]). For Ag(110) the dispersion parameters differ from the results obtained by Rocca et al. by HREELS [8], as the linear coefficient came out smaller and the quadratic term larger. Indeed, the ELS–LEED values compare better with the HREELS results of Lee et al. [12], although the smaller error rules out their conclusion that the term responsible for the anisotropy might be the quadratic one (generally assumed to be connected to bulk properties).

Contrary to the present results, the surface plasmon dispersion coefficients derived by $\chi^2$-analysis from Eq. (2) are as follows:

<table>
<thead>
<tr>
<th>Face</th>
<th>Azimuth</th>
<th>$\hbar \omega_{\text{sp}}(0) \text{ (eV)}$</th>
<th>$A \text{ (eV } \text{Å)}$</th>
<th>$B \text{ (eV } \text{Å}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>$\langle 001 \rangle$</td>
<td>$3.701 \pm 0.002$</td>
<td>$0.59 \pm 0.05$</td>
<td>$3.5 \pm 0.3$</td>
</tr>
<tr>
<td>(110)</td>
<td>$\langle 110 \rangle$</td>
<td>$3.704 \pm 0.002$</td>
<td>$0.21 \pm 0.03$</td>
<td>$3.6 \pm 0.2$</td>
</tr>
<tr>
<td>(111)</td>
<td>$\langle 111 \rangle$</td>
<td>$3.701 \pm 0.001$</td>
<td>$0.43 \pm 0.02$</td>
<td>$3.4 \pm 0.1$</td>
</tr>
</tbody>
</table>
Fig. 3. Surface plasmon dispersion curves measured on the different low Miller index surfaces of Ag at $T=90 \text{ K}$ ($T=100 \text{ K}$ for Ag(100)). The curves for Ag(110) and Ag(111) are the best fit obtained by ELS-LEED measurements, whereas the dispersion on Ag(100) was measured by HREELS [7].

The recently developed ELS-LEED has been applied to the study of the surface plasmon on the silver surfaces Ag(111) and Ag(110). The better momentum resolution allowed us to conclude that $\omega_{sp}(q=0)$ is the same for the three low Miller index surfaces of Ag and that the dominant coefficient of the dispersion for small $q$ is linear and positive, larger for Ag(110)<001> than for Ag(111) and along Ag(110)<110>. The quadratic term is the same for all the three cases and indicates that the anisotropy in the dispersion does not depend on bulk properties.

5. Conclusions

The recently developed ELS-LEED has been applied to the study of the surface plasmon on the silver surfaces Ag(111) and Ag(110). The better momentum resolution allowed us to conclude that...