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Surface plasmon dispersion of Cl/Ag(111)

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High-resolution electron-energy-loss spectroscopy has been employed to measure the dispersion of the surface plasmon on Ag(111) as a function of Cl coverage. The initial dispersion near $q_{\|}=0$ is found to shift from positive at low Cl coverages to negative as the Cl coverage approaches one monolayer. This effect is explained qualitatively in terms of the positive charging of the Ag substrate and the plasmon screening caused by the Cl overlayer. [S0163-1829(97)52432-5]

Considerable progress has recently been achieved in the understanding of the collective electronic excitations at metal surfaces.[1,2] High-resolution electron-energy-loss spectra are now available on several simple metals,[3,4] on Ag,[5] Hg,[6] Pd,[7] and on alkali-metal overlayers.[8] Calculations based on the time-dependent local-density approximation (TDLDA) (Ref. 9) indicate that the $q_{\|}$ dispersion of the monopole and multipole surface plasmons of simple metals is rather well described in terms of the excitations of the semi-infinite jellium model.[2,3,10] In the case of Ag, the *s-d* polarization was shown to give rise to a $q_{\|}$-dependent blue shift[11] which makes the dispersion positive even at small $q_{\|}$. This is in contrast to the negative initial slope found on all simple metals.[3,4,12]

The aim of this paper is to report a striking effect on the Ag surface plasmon due to the adsorption of submonolayer and monolayer coverages of Cl. The essential result is that the Cl coverage controls the initial dispersion coefficient, shifting it from the *positive* dispersion characteristic of clean Ag (111) to *negative* dispersion, characteristic of the alkali metals, as the Cl coverage increases. At larger $q_{\|}$, the dispersion remains positive. This is one of the most dramatic effects yet observed in the electron-energy-loss spectroscopy (EELS) spectra of surface plasmons. This reversal of the sign of the initial dispersion can be qualitatively explained by accounting for the charge transfer between Ag and Cl and the dielectric screening of the surface plasmon induced by the overlayer. Both mechanisms give rise to a strongly q-dependent red shift which may lead to a minimum in the dispersion curve.

The experiments were performed in a diffusion-titanium sublimation pumped ultrahigh-vacuum system with a base pressure of $\sim 5\times 10^{-11}$ Torr. The main chamber houses a four-grid retarding field analyzer for low-energy electron diffraction (LEED) and Auger measurements and an LK2000 high-resolution electron-energy-loss spectrometer. The residual gas components are monitored by a quadrupole mass spectrometer. The electron-energy-loss spectrometer consists of a double monochromator and a single analyzer as described previously.[13] The system resolution of the spectrometer can be set below 5 meV. However, since the width of the plasmon peak is of the order of a few hundreds of meV, the resolution was degraded to 20 meV in order to obtain higher signal intensity. Two primary electron energy ranges were used in the measurements and are referred to here as low beam energy (<20 eV) and high beam energy (~ 75 eV). In the experiments, the monochromator and the analyzer were fixed, while the measurements of the plasmon dispersion were realized by rotating the sample via a goniometer.

The Ag (111) sample, 1.3 cm in diameter, was cut and mechanically polished to give a mirrorlike finish. The azimuthal orientation of the surface, predetermined by Laue back diffraction, was carefully adjusted to be in the desired $[\overline{1}\,\overline{1}\,2]$ direction (within 1°) by observing the LEED pattern. The *in situ* cleaning procedure consisted of $\mathrm{Ar}+$ bombardment and annealing at 800 K before each experimental run. This procedure always resulted in an excellent LEED pattern. The surface cleanliness was monitored by Auger spectroscopy until no impurity trace could be seen. The Cl gas used in this work was obtained from Air Products Co. and was 99.9% pure. It was dosed onto the sample through a variable leak valve at room temperature. The background pressure of Cl was kept below 2×10^{-7} Torr in the chamber. No annealing was performed after the sample was exposed to the Cl gas. The chlorine concentration on the surface was obtained from the Auger peak-to-peak height ratio of Cl (182 eV) to Ag (352 eV). The plasmon measurements were carried out at various Cl coverages from 0% to approximately a monolayer.[14] The corresponding LEED patterns observed were similar to those reported by Bowker and Waugh.[15] Briefly, at low Cl coverages, the LEED pattern was (1×1) with gradually increasing background. At the saturated coverage, the LEED spots were sharp again, which corresponded to pattern ‘‘C’’ mentioned in the literature.[15] In between, the LEED pattern displayed was $(\sqrt{3}\times\sqrt{3})R\,30°$ when the coverage exceeds 2/3, but the quality was not as good as that from either the clean surface or the surface at saturated coverage.

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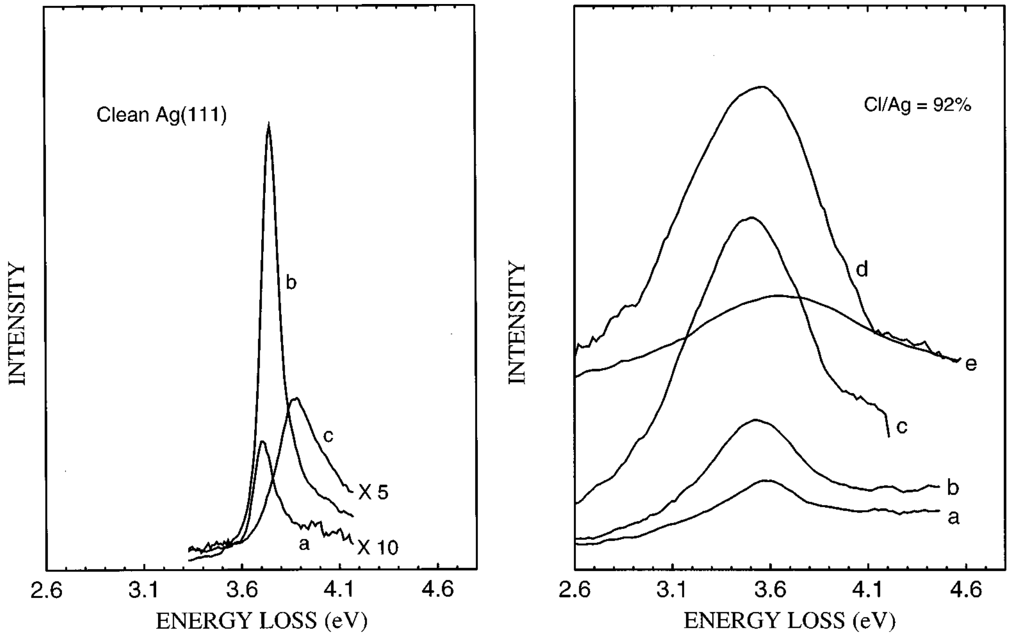

FIG. 1. Left: Electron-energy-loss spectra for clean Ag (111) at surface wave vector q along $[\overline{11}2]$ of a: -0.06, b: 0.15, and c: 0.22 Å^{-1}. The primary impact energy is 19.5 eV. Right: Electron-energy-loss spectra for Cl/Ag (111) at a coverage of 92% and for q vectors along $[\overline{11}2]$ of a: -0.01, b: 0.07, c: 0.15, d: 0.21, and e: 0.32 Å^{-1}. The primary impact energy is 14.6 eV.

The electron-energy-loss spectrum of the clean Ag (111) surface exhibits a well-defined surface-plasmon peak. Figure 1 shows the loss spectrum of the surface plasmon at various wave vectors using the primary electron energy of 14.5 eV. Overall, the measured dispersion curve is in good agreement with those reported previously, but the energies are slightly lower by 10–15 meV. At $q \sim 0$, the surface plasmon energy is 3.68 eV at room temperature, which may be compared to high-resolution electron-energy-loss spectroscopy (HREELS) data [3.69 eV (Ref. 5)] and optical data [3.65 eV (Ref. 16) and 3.68 eV (Ref. 17)]. Also shown are the loss spectra for various wave vectors near saturation coverage of Cl. As $q \rightarrow 0$, the background on the high-energy loss side increases although the plasmon peak itself narrows. In general the shape of the plasmon peak is poorest at low to intermediate Cl coverages but becomes more symmetric as the coverage increases from $\sim 45\ \%$ to saturation. This behavior qualitatively tracks the degree of ordering evidenced in the LEED patterns. The experimental data for the dispersion as a function of Cl coverage is summarized in Fig. 2. Careful analysis of the data indicates that the frequencies are accurate to within 10 meV near the specular direction and 20–30 meV in large off specular directions which either involve negative wave vectors or $q > 0.3$ Å^{-1}.

One may perform an important check on the dispersion data by repeating the measurements at substantially higher electron-beam energies. It is well known that the cross section in EELS is very sensitive to primary beam energy. Furthermore, by working at 76–78 eV primary energy, one employs very different experimental angles to access a given q vector. As illustrated in Fig. 3, the plasmon peak at saturated Cl coverage is substantially narrower in the high-energy data. This is likely due to the reduction in angular acceptance of the analyzer at higher impact energy. Figure 3 also shows the results of measurements of the dispersion for the clean surface and the Cl saturated surface at both high and low primary energies. The agreement is quite satisfactory.

The key result of this study is the change in the initial slope of the dispersion from positive to negative as the Cl coverage increases. Other features evident in the data are (i) a shift in the plasmon energy at $q = 0$ to lower energy with coverage and (ii) some asymmetry for $q \rightarrow -q$ apparent in the high coverage regime. The latter effect is likely due to a

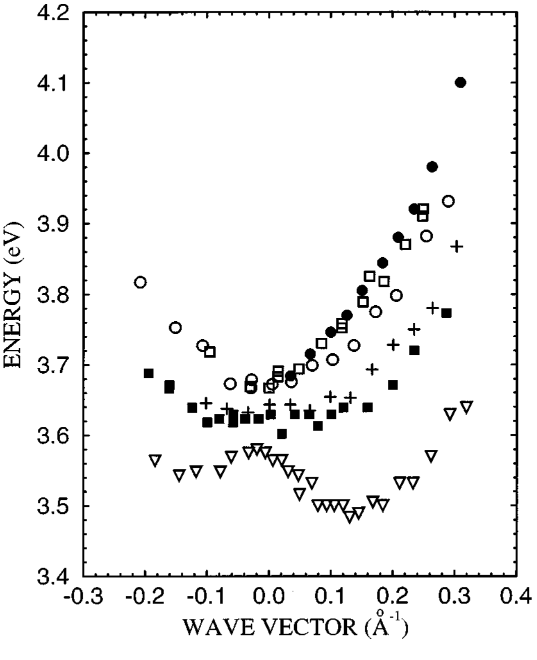

FIG. 2. Summary of surface-plasmon dispersion for the Cl/Ag (111) system as a function of Cl coverage along the $[\overline{11}2]$ azimuth. The data were obtained at low primary impact energies 14.5–19.5 eV. The corresponding Cl coverages are: clean Ag (●), 26% (□), 44% (○), 62% (+), 73% (■), and 92% (∇).

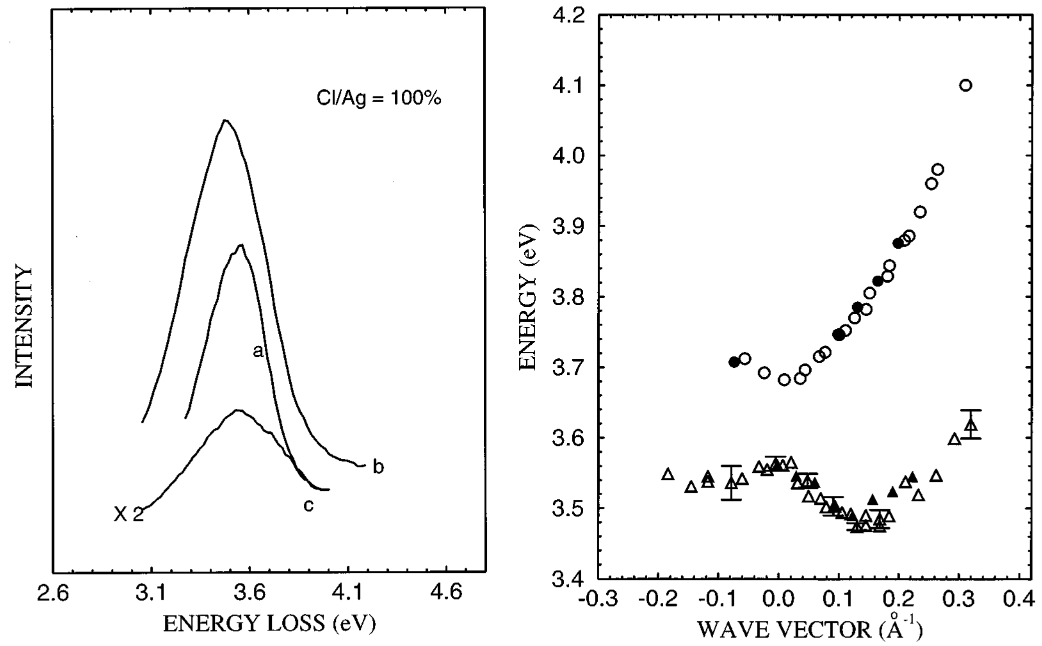

FIG. 3. Left: Electron-energy loss spectra for Cl/Ag (111) at saturation coverage and for q vectors along $[\overline{1\,1\,2}]$ of a: 0.06, b: 0.12, and c: 0.22 Å^{-1}. The primary impact energy is 78 eV. Right: Comparison of surface-plasmon dispersion curves for clean Ag (111) and Cl/Ag (111) obtained at low (open symbols) and high (shaded symbols) impact energies. Error bars are indicated at representative q vectors.

larger error in the $-q$ data due to lower intensity and large-angle scattering in the experimental setup. The former may be related to the finite acceptance of the detector which causes an averaging over q, giving an upward (downward) shift for a positive (negative) dispersion near $q=0$. The presence of defects, steps, etc., tends to enhance this effect since it implies the admixture of finite q components. Dissolution of Cl$^-$ ions into the bulk should also lower the plasmon frequency.

The modification of the Ag surface-plasmon dispersion due to the adsorption of Cl can be qualitatively understood via a generalization of the *s*-*d* polarization model proposed earlier by Liebsch.[11] In this scheme the dynamical response of the 5*s* electrons is treated within the jellium model and the influence of the occupied 4*d* bands is described in terms of a polarizable medium that screens the Coulomb interaction between the conduction electrons. The dielectric function $\epsilon_d(\omega)$ of this medium is obtained from the bulk dielectric function by writing $\epsilon(\omega)=\epsilon_s(\omega)+\epsilon_d(\omega)-1$, where $\epsilon_s(\omega)=1-\omega_p^2/[\omega(\omega+i\gamma)]$ with $\omega_p=9.2$ eV. The medium is terminated at the distance z_d from the jellium edge. The Ag surface-plasma frequency at $q=0$ is given by $\omega_s^* =\omega_p/\sqrt{1+\epsilon_d}\approx 3.7$ eV.

Because of the spill out of the *s* electron density, a part of the fluctuating plasmon charge is located outside the *d* electron medium and is therefore not exposed to the *s*-*d* screening. This spill-out effect shifts the frequency up towards the unscreened plasma frequency. At small q, the shift is small because of the slow decay of the plasmon field. With increasing q, however, the blue shift increases since the plasmon field decays more rapidly and the *s*-*d* polarization becomes less effective. TDLDA calculations[11] show that, for reasonable choices of z_d ($\approx -1\ a_0$), the blue shift outweighs the standard red shift at small q that is seen on all simple metals.

To interpret the Cl/Ag data we extend the above model in the following manner: We assume the charge transfer from Ag to Cl to be limited to the Ag 5*s* electrons which are treated as a semi-infinite but charged jellium system. The dielectric medium representing the *d* bands remains unaffected by the adsorption. The transferred electrons occupy more tightly bound Cl *p* levels[18] and do not take direct part in the plasmon oscillation. However, since the Cl *p* shells enhance the screening of the plasmon, we add a thin slab with dielectric constant ϵ_a in the region $0\leqslant z\leqslant a$, where $a/2\approx 3.4\ a_0$ corresponds to the ionic radius of Cl$^-$. The details of the theoretical approach will be given elsewhere.[19]

Figure 4 compares the dispersions derived from TDLDA calculations for neutral Ag and Cl/Ag. To illustrate the effect of adsorbate-induced surface charging and dielectric screening, we choose the extreme case where every Ag surface atom donates 0.5 electron to the Cl layer. At a full monolayer, there are about 2 Ag surface atoms per Cl atom. Thus, the surface charge is $\sigma\approx 0.02$ a.u. From the atomic polarizability of Cl$^-$, $\alpha\approx 3$ Å^3,[20] we find $\epsilon_a\approx 2$. The presence of the Cl layer is seen to cause an appreciable red shift at finite q, so that the dispersion now exhibits a minimum. In order to show the relative importance of the physical mechanisms, we also give the dispersions for pure surface charging and pure dielectric screening. The results indicate that most of the red shift is due to the screening action of the Cl overlayer.

While the red shift associated with the dielectric overlayer is plausible, the red shift due to positive charging is surprising and opposite of what is found for charged jellium surfaces.[21] This may be understood as follows. Positive charging modifies the *s* electron density in two ways: it leads (i) to a steepening and (ii) to an inward shift of the profile. The steeper density is less polarizable so that higher density regions must be involved in the surface screening processes. This effect increases the plasma frequency. The inward shift, on the other hand, pushes the fluctuating surface charge to-

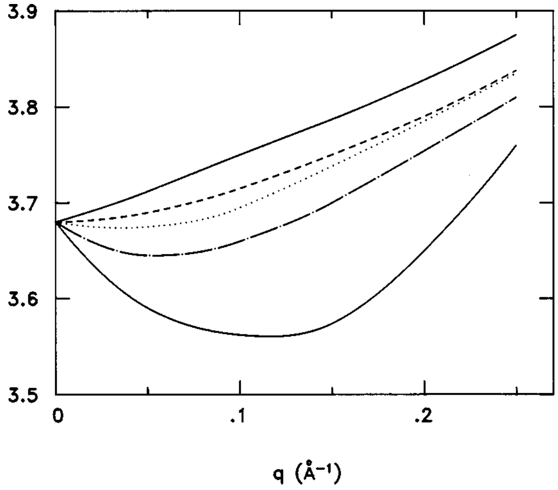

FIG. 4. Dispersion of Ag surface plasmon as calculated within TDLDA. Upper solid curve: clean, neutral Ag; dashed curve: charged Ag ($\sigma = 0.02$ a.u.); dotted curve: neutral Ag with dielectric overlayer ($\epsilon_a = 2$); dot-dashed curve: charged Ag with dielectric overlayer. Lower solid curve: dispersion for neutral Ag with dielectric surface layer corresponding to AgCl ($\epsilon_a = 4$). The boundary of the dielectric background representing the d electrons is $z_d = -1.2$ a_0 in all cases.

wards the 5d electrons and enhances the s-d polarization. The TDLDA calculations show that the red shift due to this reduced spill out is much stronger than the blue shift due to the stiffer density. In fact, whereas the blue shift quickly saturates with increasing positive charging, the red shift continues to grow and only ceases when the plasmon charge is shifted deep inside the d electron medium.

Since microscopic chemisorption calculations for Cl on Ag(111) are not yet available, the exact charge transfer is not known. Most likely, it is smaller than assumed above. Hence, the red shift of the surface plasmon should be less pronounced. On the other hand, since the data were taken at room temperature, dissolution of Cl into the substrate is likely to occur.[15] This should give rise to additional screening effects that modify the plasmon dispersion. For illustrative purposes we also show in Fig. 4 the dispersion for neutral Ag in the presence of a thin dielectric layer with $\epsilon_a = 4$, corresponding to bulk AgCl. The red shift of the plasmon at finite q is in this case even more pronounced than for charged Ag covered by a Cl$^-$ layer, giving a correspondingly deeper minimum in the dispersion curve. The comparison with the measured dispersions shown in Figs. 2 and 4 suggests that realistic Cl/Ag(111) surfaces presumably involve contributions from all three mechanisms: surface charging, plasmon screening via the Cl overlayer, and screening via surface alloy formation.

In summary, the adsorption of Cl provides a unique way of modifying the surface electronic properties of Ag in a controlled fashion. At a full monolayer, the data reveal a remarkable sign change of the initial slope of the Ag surface-plasmon dispersion. We have shown that both the positive charging of the Ag substrate and the screening effect of the overlayer lead to a substantial red shift of the surface-plasma frequency at finite q. It would be interesting to measure the dispersion at low temperatures since the formation of an AgCl surface alloy should then be predominant at high exposures. Also, adsorption of rare-gas layers instead of Cl would suppress surface charging and would enable one to focus on the overlayer-induced plasmon screening. Finally, adsorption of Cl or rare-gas atoms on Ag(001) should reveal a weaker red shift since the dispersion on the clean face is more strongly positive. One of us (J.K.) acknowledges the support of the Korean Science and Engineering Foundation through Atomic Scale Surface Science Research Center.

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