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Abstract

Surface-sensitive spectroscopic techniques, namely metastable deexcitation spectroscopy (MDS) and ultraviolet photoemission (UPS), have been applied to investigate the effects of chlorine chemisorption on the electronic properties (surface density of states and charge density) of Ag(100), Ag(110) and Ag(111) surfaces. Initial stages of chemisorption, up to the formation of a saturated Cl overlayer, have been examined. In particular, MDS permitted us to observe at low Cl gas exposure a progressive depletion of the Ag (5s) charge due to transfer and bonding with Cl atoms. From both MDS and UPS it was possible to observe the development of Cl (3p) bonding and anti-bonding states, the amount of their splitting increasing with coverage. Differences between chemisorption at the three surfaces have been noticed and they have been justified in terms of the different adatom packing and possible formation of small AgCl clusters (especially for the Ag(111) surface).

1. Introduction

The aim of the present work is the experimental investigation of the evolution of the surface density of states (SDOS) and surface charge density (SCD) of silver single-crystal surfaces upon chlorine exposure.

Adsorption of chlorine on silver has been the subject of intense study in the last decade [1–12], principally due to the importance of this system in the promotion of the selective oxidation of ethylene. The origin of the increase of selectivity with chlorine coverage, which occurs at around 0.4 monolayers, has been related to the presence of Cl-induced states near the Fermi energy, leading to a reduced interaction of oxygen with the substrate (favouring the reaction with ethylene) [8–12].

Moreover, recent studies on positive ion neutralization and negative ion scattering at Cl-covered Ag surfaces [7, 13] have reported on an interesting oscillating behaviour in the Auger neutralization and resonant electron transfer rates during the initial stages of adsorption, where changes in catalytic selectively occur. These variations were ascribed to different adsorption phases within the first Cl overlayer, causing a progressive modification of SCD and SDOS and consequently a modification in the electron transfer processes.

It is evident that the availability of detailed information on the surface electronic states associated with the adsorbate is a key factor for the understanding of these phenomena. To this aim we applied metastable atom deexcitation spectroscopy (MDS), which is an extremely surface-sensitive technique [14], to investigate the evolution of the surface valence band (VB) at increasing chlorine exposures. The study is focused on the earliest exposure regimes, ranging from 0 to 3.5 Langmuir of Cl_2, extending somewhat above monolayer formation. The effects of chlorine exposure have been systematically investigated on all the three high symmetric (100), (110) and (111) low Miller index surfaces of silver.

From structural studies it is known that on clean Ag surfaces chemisorption of halogens produces ordered overlayers. On Ag(100) a c(2 × 2) saturation phase has been found at a coverage of 0.5 monolayers (ML—expressed in terms of the substrate surface atoms) [15, 16]. On Ag(110) and Ag(111) several structures have been observed depending on coverage. On Ag(110) an initial p(2 × 1) phase at about 0.5 ML evolves into a c(4 × 2) pattern at about 0.75 ML [15, 16]. On Ag(111) initial chlorine coverage gives rise to a ($\sqrt{3} \times \sqrt{3}$)-R 30° pattern [17, 18]. This evolves into a (17 × 17) saturation structure at higher doses [1, 3]. Further dosing of Cl_2 causes the formation of AgCl patches at the surface.

In MDS slow noble gas atoms in a metastable excited electronic state (in this work He*) deexcite at the surface as a consequence of the overlap between atomic and solid wavefunctions. Since deexcitation, involving electrons from the surface VB, takes place outside of the surface, unique information on SDOS and SCD can be achieved. In particular, as far as the surfaces of noble metals are concerned, MDS matrix elements involve enhanced sensitivity to those sp electronic states, close to the Fermi edge, which most protrude into the vacuum. These sp electrons play a fundamental role in atomic and molecular interaction with the solid, adsorption processes and surface chemical reactions. In this perspective, the obvious importance of the information coming from MDS in the study of ion neutralization at surfaces and in related techniques has been known for a long time, especially after the seminal investigation of Hagstrum in the 1950s [6, 7, 13].

The MDS analysis has been flanked by angle-resolved ultraviolet photoemission (AR-UPS). Because of their different sensitivities to different contributions of the surface electronic structure, the joint use of MDS and UPS helps in clarifying the modifications of the density of states as adsorption changes from smaller to higher packing of adsorbed Cl atoms. Moreover, important information regarding adsorbate–adsorbate and adsorbate–substrate interactions during the different phases of chemisorption can be accessed.

2. Experimental details

MDS and AR-UPS measurements were performed in a multi-technique apparatus, described in [19]. The base pressure was below 10^{-10} Torr.

A gas discharge supersonic source [20] was used to produce a beam of mainly (∼90%) triplet 2^3S metastable He atoms.

The He* flux on the surface was of the order of 10^{11} atoms s^{-1} operating the source at 400 V and 20 mA. The beam impinged on the sample at an angle of 45° with respect to the sample normal. The emitted electrons were analysed at 45° with respect to the surface

normal with a hemispherical analyser (VG ADES 400) with a 0.3 eV energy resolution. An ultraviolet source equipped with a linear light polarizer (VG) was used for He I photoemission ($h\nu = 21.2$ eV). The polarizer ensures a 90% light polarization [21].

Commercial Ag monocrystalline samples were polished to 0.05 μm and oriented to within 0.5°. *In situ* preparation was accomplished by cycles of Ar$^+$ grazing sputtering and annealing, as described elsewhere [6, 7, 13]. Surface order and cleanliness were ascertained by LEED/Auger and UPS/MDS analysis.

Because chlorine adsorption proceeds rapidly when Cl$_2$ gas is used, an admixture of Ar with pure Cl$_2$ was employed, in order to obtain an easier control of the exposures [22]. The exposures (expressed in Langmuirs, with 1 L $= 1 \times 10^{-6}$ Torr s) using pure gas and the admixture were related to each other through work function (WF) variation measurements. In the following, results will be presented as a function of pure Cl$_2$ exposure values.

Monitoring WF variations represents a convenient way to control Cl$_2$ adsorption. The WF variations were measured by analysing the position of the low kinetic energy cut-off of the secondary electrons in He I photoemission and metastable deexcitation spectra, with a -5 V bias applied to the sample. WF variations were related to Cl$_2$ exposures with reference to the calibration reported in [13].

Chlorine adsorption on silver induces a strong increase in the WF. The WF changes turned out to be similar for all three surfaces. The WF increases rapidly, by a total amount of 1.6–1.8 eV, reaching a saturation value at about 1.5 ± 0.3 L, in good agreement with previous measurements [17, 23, 24].

The experiments were performed at room temperature.

3. Results

3.1. MDS

MDS spectra measured after Cl$_2$ exposure up to 1.2–1.5 L are reported in figures 1(a)–(c) for the three Ag surfaces. In order to emphasize and compare the adsorbate-induced features, the first derivatives (FD) of the distribution curves are also shown in panels 1(d)–(f). At higher exposures, in the range investigated here, no further spectral changes were observed.

The clean Ag surfaces spectra present, when looking at the spectra from higher towards lower kinetic energies (KE), a typical three-step lineshape. This lineshape is associated with the occurrence of the so-called resonance ionization (RI) of He* (He* $\rightarrow$ He$^+$) followed by an Auger neutralization (AN) process of the resulting ion (He$^+$ $\rightarrow$ He). Under several approximations [14, 25–27], this type of spectrum can be viewed as an autoconvolution of the SDOS (SDOS*). In this respect, it displays a so-called *band-like* character. Here the notation SDOS* is intended to emphasize the *effective* character of this density of states, as the actual SDOS is weighted by the AN matrix element. The high KE onset (corresponding to the high KE peak in the FD) is related to the folding of the sp part of the SDOS*(sp*sp) of silver while the second step (FD peak at 9.5 eV KE) can be ascribed to the convolution of the sp part with the d levels (sp*d).

The nature of the third step at about 5 eV KE, which might be related to some extent to a convolution of the d states (d*d), is more controversial, both due to the influence of the secondary emission increasing at low KE and of possible *atomic-like* contributions. Its nature will be addressed in more detail elsewhere [28].

As adsorption of Cl proceeds, the metal-related structures are severely attenuated. Dramatic modifications are observed for all surfaces, already at very modest exposures (0.1–0.3 L).
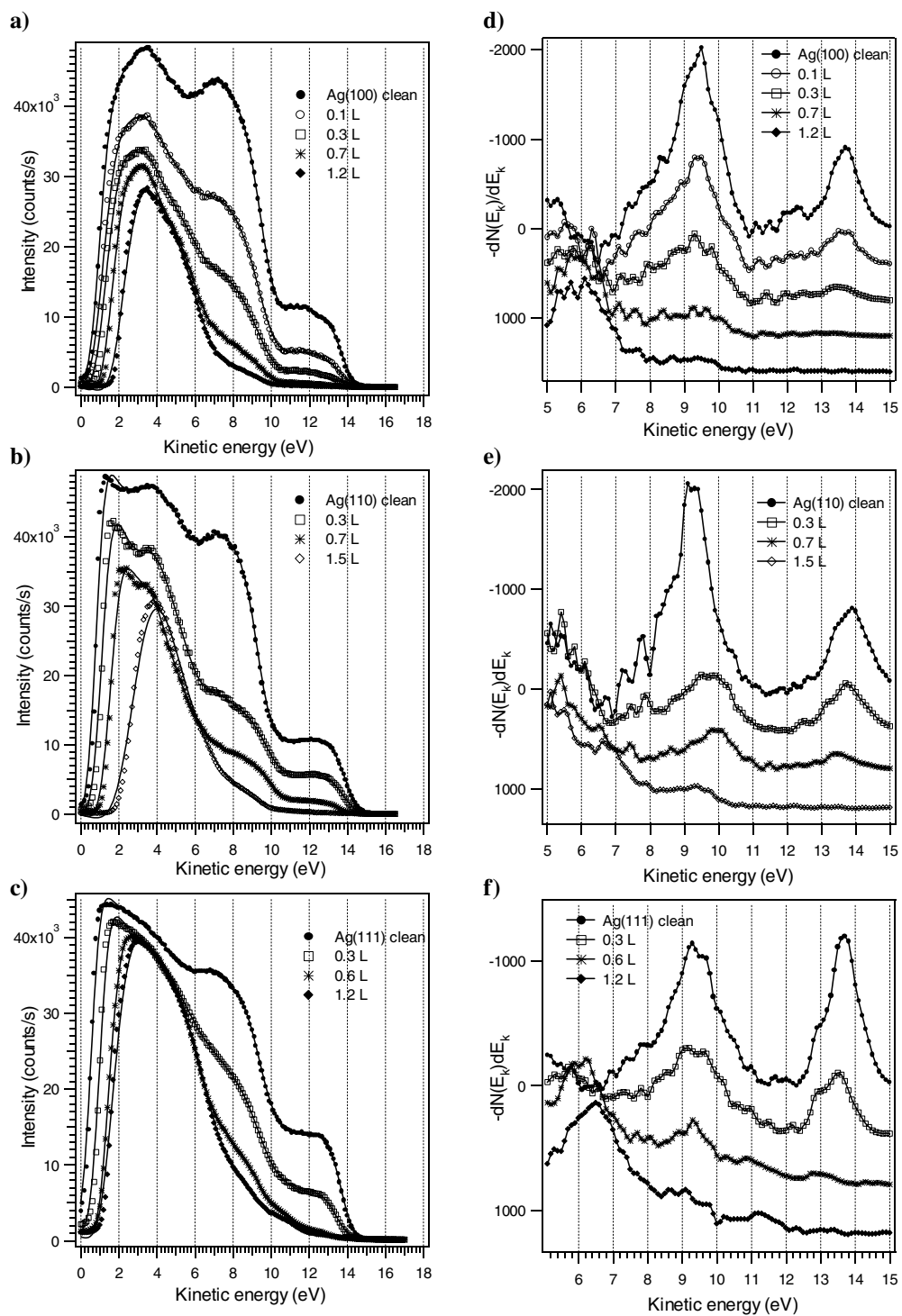
Figure 1. In panels (a)–(c) the metastable deexcitation spectra (symbols), together with spline filtering of the data, are shown for the three Ag(100), Ag(110) and Ag(111) surfaces, respectively, as a function of chlorine exposure. In panels (d)–(f) the corresponding FD of the spectra are reported. Curves have been arbitrarily displaced for visualization purposes.

The occurrence of AN *band-like* spectra at lower exposures justifies the calculation of deconvolutions to obtain information on the SDOS* [14, 26, 27]. Deconvolution curves were calculated only for the exposure ranges where a clear sp*sp related structure was observed at high KE (below 1 L). The deconvolution results obtained after spline filtering of the spectra (full curves in figures 1(a)–(c)) are shown in figures 2(a)–(c).

The deconvolution curves are reported as a function of the binding energy (BE), referenced to the high KE onset. This is related to emission from the Fermi edge [14] at 14.6 ± 0.3 eV on direct spectra, the uncertainty being mainly due to the high energy tail broadening.

Two main features can be observed in the deconvolution curves of the clean Ag surfaces. The first one (at about 0.5 eV BE) is associated with the sp-type DOS; the second, ranging approximately from 3.5 to 7.5 eV BE, is associated with the Ag (4d) band [28–30].

At large exposures, smooth, relatively structureless spectra are observed. The general trends for the Ag(100) and the Ag(110) cases appear very similar. In the Ag(111) case the intensity decrease as a function of coverage seems less pronounced and the spectrum at saturation has a larger width than those from the other two surfaces. Furthermore, both due to the WF increase and possibly to a decrease of the He ionization energy in front of the electronegative adsorbate, the spectra become progressively narrower.

These high exposure spectra have apparently lost any features which may be related to a so-called Auger *band-like* behaviour. This fact matches with MDS observations on other electronegative saturated overlayers (such as, for example, atomic oxygen and hydroxyl chemisorbed on Ag(110)) [29, 30]. For this reason, we did not perform deconvolutions to obtain SDOS* structures at the highest exposures investigated, since these were not considered to be reliable.

Deconvolutions reported in figure 2 clearly show that the metal-related features below the Fermi energy are progressively reduced since the early stages of adsorption. The quenching of the sp part of the spectrum leads to a reduction also of the d part, which is probed by an AN process involving one sp and one d electron.

At about 0.3 L of exposure deconvolutions for the three surfaces show Cl-induced shoulders rising at both sides of the Ag(4d) feature. This is less evident for Ag(100) where contributions from Cl could be hidden below the main structure centred at about 5 eV of BE in figure 2(a). In this respect it should be noted that the intensity in the sp part decays more drastically than in the d region, suggesting that Cl-induced states are located in the latter energetic position.

For all three surfaces the sp charge quenching appears to be almost complete at about 0.7 L (look also at the FD curve of figure 1).

At about 0.7 L the Cl-induced structures increase. In particular the shoulder appearing at about 4 eV, just at the edge of the d-band of Ag, is reinforced at 0.6–0.7 L and shifts towards lower BE. This is evident in figures 2(b) and (c).

At variance with the other cases, for Ag(111) a strong structure can be noted between 7 and 8 eV BE. However, at least two reasons induce some caution in the assignment of this last structure. First, the *band-like* character of the spectrum cannot be completely assessed at this exposure.

Second, even admitting the *band-like* character, this high BE feature could be overestimated in the intensity in the deconvolution procedure due to the increasing influence of a background of secondary electrons at low KE.

3.2. Photoemission

Chemisorption of halogens on Ag surfaces has been investigated in detail using UV photoemission by Goldmann and co-workers [31, 32]. In the present work photoemission spectra have been taken at normal emission on the three Ag surfaces at increasing Cl_2 dosing.
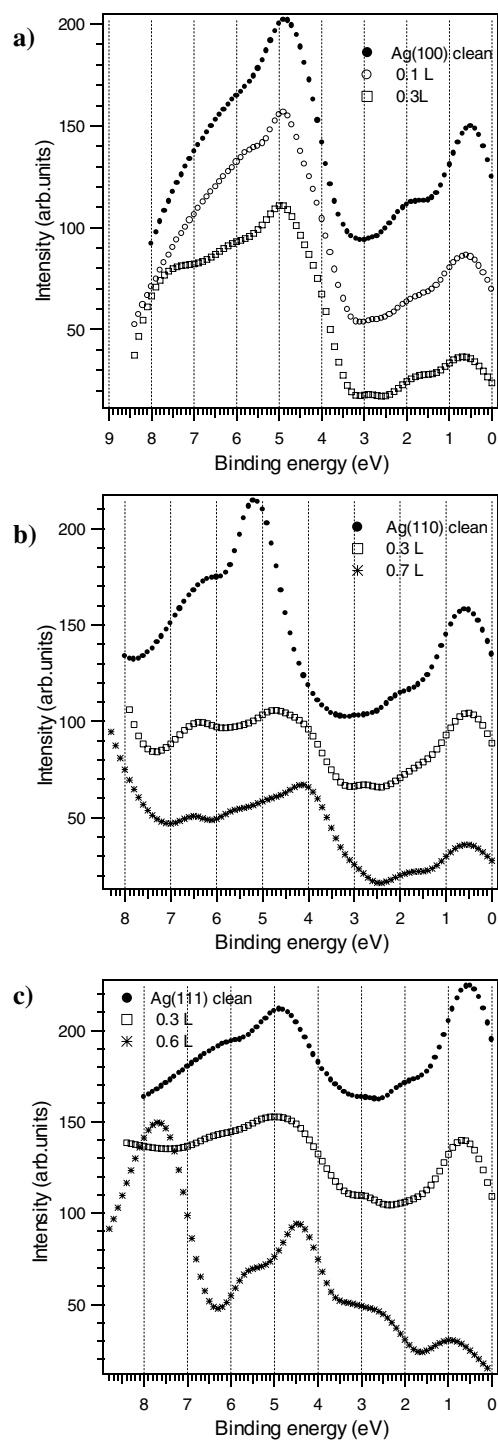
Figure 2. Deconvolutions (*effective* SDOS*) calculated as a function of chlorine exposure for the three Ag(100) (a), Ag(110) (b) and Ag(111) (c) surfaces. The step-like onset at the zero of BE is due to the deconvolution procedure. Curves have been arbitrarily displaced for visualization purposes. The intensity axis is referenced to the lower curve in each graph.

Data were taken in order to compare with MDS at comparable exposure conditions and to relate the experimental information with previous works from the literature. UPS spectra are presented in figure 3. The essential features of photoemission can be summarized as follows.

Clean Ag surfaces show a pronounced emission in correspondence of the 4d band between 3.5 and 7.5 eV BE, while only very weak structures are observed in the sp region, below 3 eV BE.

The overall spectral evolution during chlorine dosing appears to be similar on the three surfaces. Poor modifications of the spectral features of clean Ag are observed below 0.4 L, despite the significant variations in MDS spectra and the increase of the WF in this range [13]. The first evident variations occur in the range 0.4–0.7 L where the d band region is progressively modified. Finally, definite spectral shape changes occur for larger exposures (>1 L), just where the MDS spectra show negligible variation. New Cl-induced features that show up have been labelled A, B, C and D.

Comparing the three surfaces, the more pronounced differences appear on Ag(111). Above 1.4 L the Cl-induced feature at lower BE with respect to the Ag(4d) states is strengthened and splits into two contributions, at 2.7 and 3.5 eV BE, labelled A′ and A″, respectively.

In order to obtain further insights into the nature of these structures, photoemission experiments with polarized light were carried out on Ag(111).

In figure 4(b) the spectra taken at normal emission on the Cl-saturated surface are reported; clean surface spectra are reported in panel (a) for comparison.

The spectra were measured with linearly polarized light with the vector potential A perpendicular ($A_\perp$, s-type geometry) and parallel ($A_\parallel$, p-type geometry) to the plane of incidence. The photon incidence angle was 20° in both cases. In normal emission the final state ($|f\rangle$) of the photoexcitation process is totally symmetric under point group operations about the surface normal [33]. For an initial state ($|i\rangle$) symmetric with respect to the incidence plane, a non-vanishing matrix element in the dipole approximation ($\langle i|A \cdot p|f\rangle$) is obtained for p polarization. Photoemission from an antisymmetric state is allowed for $A_\perp$ (s geometry).

By looking at figure 4(b), in p geometry ($A_\parallel$) the Cl-induced features labelled by A′ and A″ are much less intense than in the spectrum taken in s geometry ($A_\perp$). These observations induce us to assign a dominant p_x, p_y character to the whole structure up to the Fermi energy. Nevertheless, some p_z-type contribution can also be observed in the $A_\perp$ spectrum at about 3 eV.

Insofar as the VB features above 4 eV of BE (the Ag(4d) band region) are concerned, p-polarized light ($A_\parallel$) emphasizes adorbate-induced electron emission between 6 and 7 eV (figure 4(b)), just where the contributions from the Ag(4d) band of the clean surface (figure 4(a)) are extremely small (with the same light polarization) due to dipole selection rules. It can be deduced that a substantial part of the electron emission intensity in this region is due to p_z-type Cl-induced states.

4. Discussion

From the data presented above it is clear that MDS and UPS present different sensitivities to the surface VB features.

Concerning MDS, the spectrum lineshape reflects the preferential interaction of the metastable atom with those surface electrons whose wavefunction spills out more into the vacuum region. MDS gives apparently its major information in the initial stages of adsorption due to its well known sensitivity to the metal sp-like contributions. Unlike UPS, this sensitivity permits us to observe with extreme clarity the progressive depletion of the Ag(5s) surface charge at very small exposures. This result has to be associated to a charge transfer from the metal to Cl-induced states due to bonding between surface and halogen atoms.

UPS starts to give major information only at relatively high exposures, just where MDS shows almost complete depletion of the sp metal band. At initial stages of adsorption (below
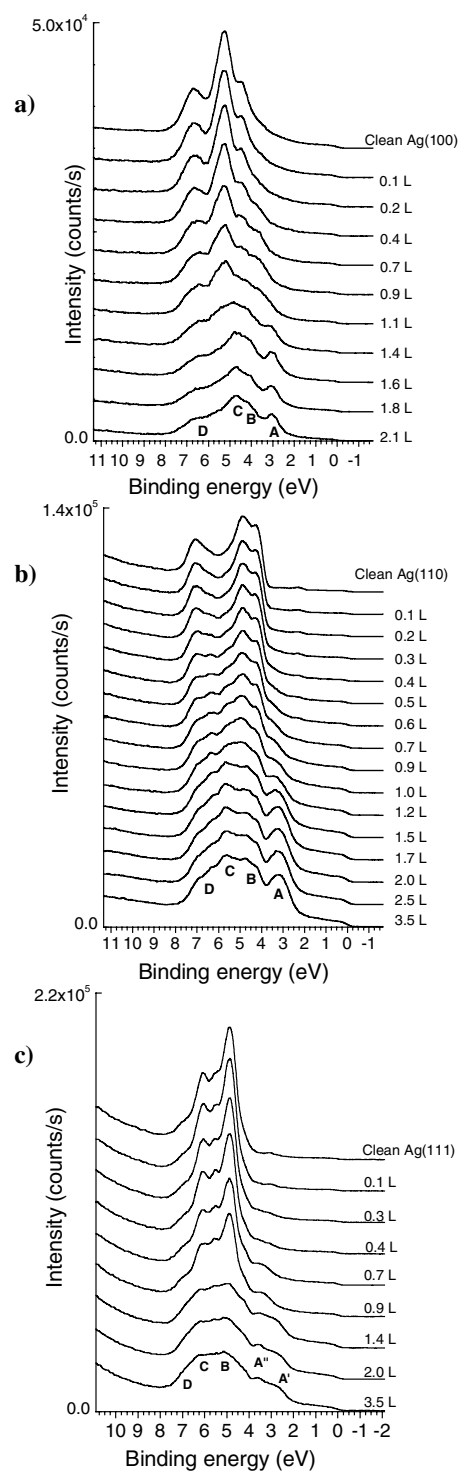
Figure 3. He I ($h\nu = 21.2$ eV) normal emission spectra taken on the three Ag(100) (a), Ag(110) (b) and Ag(111) (c) surfaces as a function of chlorine exposure. The spectra are reported as a function of BE referenced to the Fermi level position.
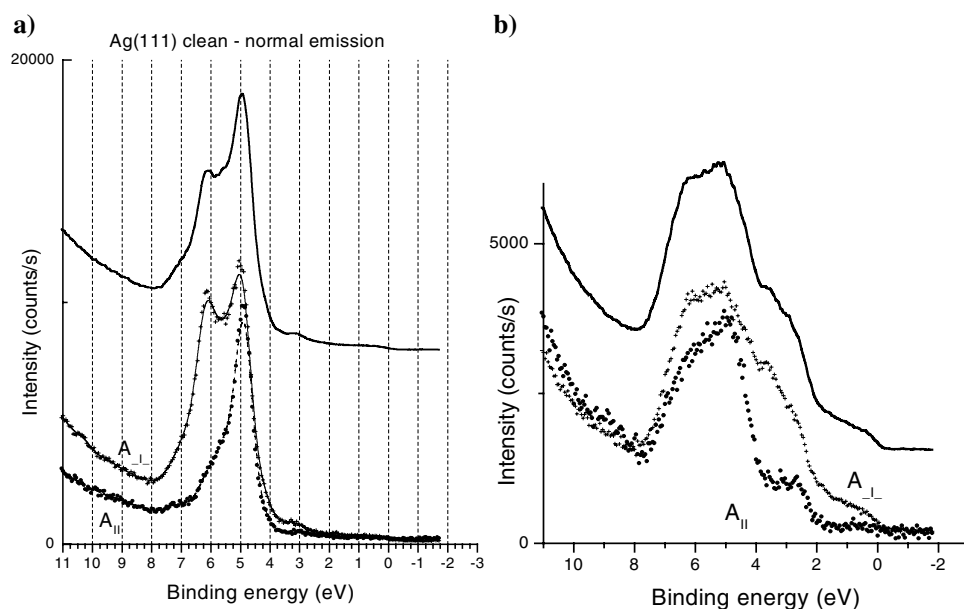
Figure 4. He ɪ($h\nu = 21.2$ eV) normal emission spectra taken with linearly polarized light in the s ($A_\perp$) and p ($A_\parallel$) geometry on the clean Ag(111) surface (a) and on the Cl-saturated Ag(111) surface (b). Thick full curves are unpolarized light spectra.

about 0.4–0.5 L), Cl-induced levels are hardly detectable in He ɪ photoemission for the three systems. As suggested by the analysis of MDS deconvolution curves at low coverage, these levels are most probably located in the energetic region of the metal d band and therefore hidden in UPS by overwhelming bulk emission.

For larger exposures, clear adsorbate-induced features become apparent in UP spectra. The features observed in the present work are in good agreement with previous UV-photoemission investigations on the chemisorption of Cl on Ag(001) and Ag(110) [31, 32].

On the basis of previous work on this system [6], and also taking into account experiments and theoretical studies on related systems such as O/Ag [29, 34] and OH/Ag [35], a major anti-bonding p character can be assigned to the peaks labelled with A. In this respect, the Ag(111)–Cl system at high coverage displays lower BE components for the anti-bonding levels (the A′ and A″ features), which can be related to the increased packing of Cl atoms at this surface compared to the other surfaces. This is consistent with SEXAFS experiments, according to which the Cl–Cl interatomic distance is 2.89 Å on Ag(111) at saturation coverage [36], which increases to 3.14 Å on Ag(110) [37] and to 4.06 Å on Ag(100) [38].

A $p_{x,y}$ character was previously assigned to the anti-bonding Cl levels on the basis of comparison with a model calculation of the dispersion of the 3p band for a free standing layer of chlorine [32]. This is consistent with recent VB calculations [39], which predict also that contributions from p_z-type states are spread over the entire VB region. Our observations appear to be in substantial agreement with the literature, as polarized light experiments on Ag(111) indicate a dominant $p_{x,y}$ character of the A (A′ + A″) structure. However, some contribution is also observed from p_z-type levels, mainly related to the A′ feature.

The VB features above 4 eV of BE (B, C and D) are associated with strongly hybridized Cl(3p)–Ag(4d) states, most probably of bonding character. Polarized photoemission on Ag(111) shows that a considerable part of the electron emission intensity in the region between 6 and 7 eV is due to p_z-type states.

An interesting aspect, common to all three surfaces in UPS, is the small but sizeable increase of emission in the region between 2 and 0 eV BE at increasing coverage. This can be related to the spread of the Cl(3p) bonding charge over the entire VB region, including some contributions up to the Fermi level, as theoretically predicted in [34, 39, 40].

MDS shows saturated smooth, structureless patterns at exposures ranging from about 0.7 to 1 L, where UPS shows a nice spectral dynamics.

In this respect, it is well known that, on insulating systems, the so-called Auger deexcitation (AD) process should prevail over the RI + AN mechanism, since no empty states are available to activate the resonant ionization (RI) channel. AD generally induces 'single'-electron 'UPS-like' spectra [14].

Considering the excitation energy values for He I (21.22 eV) and 2^3S He (19.8 eV) and the photoemission results of the previous section, AD should induce a sizeable 'UPS-like' emission in a region ranging approximately from 11 to 15 eV of KE.

Inspection of the high coverage spectra of figures 1(a)–(c) and FD of figures 1(d)–(f) shows that these effects are almost negligible and RI + AN apparently remains the dominating deexcitation channel. For a closer comparison, a zoom into the high KE onset region of the MD spectra is shown in figure 5. The spectrum at Cl saturation exposure on Ag(111) is broader than the corresponding spectra on the other two surfaces and it reveals some weak structures whose energy position could be assigned to Auger deexcitation. In particular a small but definite onset is visible at about 15 eV of KE.

The occurrence of AD on the saturated Ag(111) surface could be associated to deexcitation on insulating (chloride) patches, which STM has shown to be present on the surface at these exposure ranges [3]. This behaviour would differ from the other surfaces where higher Cl_2 exposures are needed to obtain AgCl. However, it is indeed difficult to correlate the observed weak AD emission to features of the AgCl VB structure.

Indeed, the full interpretation of high coverage spectra needs further theoretical insights of the dynamics of metastable deexcitation in front of a metal surface covered with an electronegative adsorbate.

5. Conclusions

The chemisorption of chlorine on the three different high-symmetry low Miller index surfaces of silver was studied, following and comparing the evolution of the VB electronic properties by metastable deexcitation spectroscopy (MDS) and photoemission (UPS). These two techniques are complementary and permit us to access different orbital contributions of the SDOS.

Upon chlorine chemisorption in the 0–3.5 L range, the three surfaces show an overall similar behaviour, both concerning MDS and UPS.

The MDS signal shows the strongest modifications at very small exposures, where no lineshape variation can be appreciated by photoemission. In contrast, at higher exposures, while MDS spectra present a progressive saturation effect on the lineshape, photoemission shows the growth and evolution of the 3p Cl bonding and anti-bonding states at both sides of the Ag(4d) emission.

The modification of the MDS signal at small coverage is ascribed to the progressive depletion of the Ag(sp) states just below the Fermi energy, associated principally to the charge transfer to the chemisorbed chlorine atoms. This effect is not observed clearly by photoemission, which, on the other hand, emphasizes the development of Cl(3p) anti-bonding and bonding features, appearing at the low and high BE side of the Ag(4d) band at higher coverage. The strengthening of the Cl–Cl interactions at high exposures corresponding to the formation of a saturated Cl overlayer is evidenced by a larger separation between bonding and
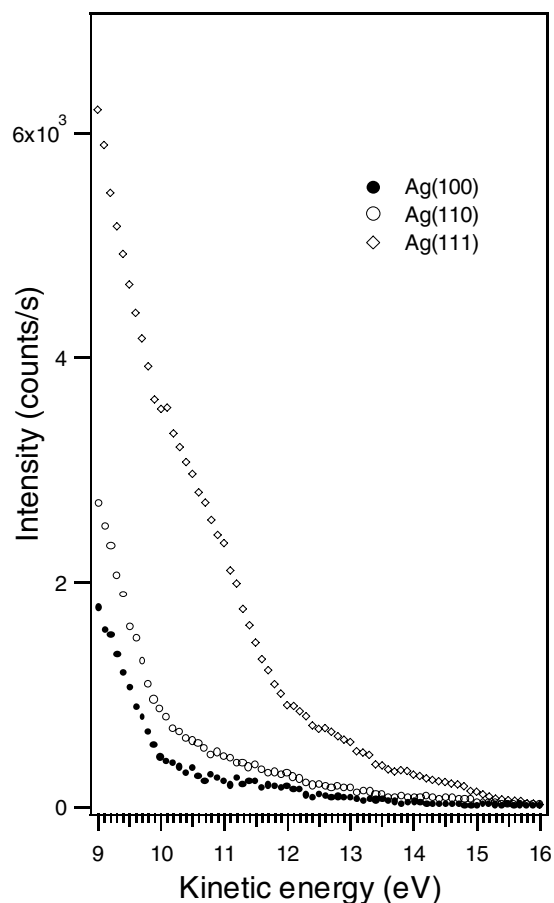
Figure 5. Comparison of the high kinetic energy electron emission obtained in MDS for the three Cl-saturated Ag surfaces.

anti-bonding Cl(3p) states, with the anti-bonding features shifting towards lower BEs. The similar trends shown by the different surfaces can be ascribed to a similar chemical state of the different surfaces at comparable Cl coverage. This indicates that the major contributions to the VB originate from the Ag–Cl interaction, which is not strongly influenced by the particular chemisorption geometry and crystal surface, as expected for ionic character bonding.

Comparing the three Ag(100)–Cl, Ag(110)–Cl and Ag(111)–Cl systems, the last one shows the more pronounced differences. The Cl(3p) anti-bonding feature at saturation coverage is more evident with respect to the other cases and appears at lower BE. These findings are related to the increased Cl–Cl lateral interaction with respect to the other surfaces, caused by the reduced adatom interatomic distance.

Some peculiar features of the MDS spectrum of Ag(111) at the highest exposures investigated could be related to the formation of AgCl islands at the surface.

Acknowledgment

References

[1] Andryushechkin B V, Elstov K N, Shevlyuga V M and Yurov V Yu 1998 *Surf. Sci.* **407** L633
[2] Andryushechkin B V, Elstov K N and Shevlyuga V M 1999 *Surf. Sci.* **433–435** 109
[3] Andryushechkin B V, Elstov K N, Shevlyuga V M and Yurov V Yu 1999 *Surf. Sci.* **431** 96
[4] Andryushechkin B V, Elstov K N and Martynov V V 1995 *Phys. Low-Dim. Struct.* **6** 1–10
[5] Andryushechkin B V, Elstov K N, Shevlyuga V M, Tarducci C, Cortigiani B, Bardi U and Atrei A 1999 *Surf. Sci.* **421** 27
[6] Staicu-Casagrande E M, Guillemot L, Lacombe S, Esaulov V A, Canepa M, Mattera L, Pasquali L and Nannarone S 2000 *J. Chem. Phys.* **113** 2064
[7] Staicu-Casagrande E M, Lacombe S, Guillemot L, Esaulov V A, Pasquali L, Nannarone S and Canepa M 2001 *Surf. Sci.* **480** L411
[8] Serafin J G, Liu A C and Seyedmonir S R 1998 *J. Mol. Catal.* **131** 157
[9] van Saten R A and Kuippers H P C E 1987 *Adv. Catal.* **35** 265
[10] Grant R B and Lambert R E 1985 *J. Catal.* **92** 364
[11] Jorgensen K A and Hoffman R 1990 *J. Phys. Chem.* **94** 3046
[12] van den Hoek P J, Baerdens E J and van Santen R A 1989 *J. Phys. Chem.* **93** 6469
[13] Guillemot L, Staicu-Casagrande E M, Lacombe S, Esaulov V A, Pasquali L, Nannarone S, Canepa M, Vargara L and Grizzi O 2001 *Nucl. Instrum. Methods* B **182** 41
[14] Hagstrum H D 1988 *Chemistry and Physics of Solid Surfaces VII* ed R Vanselow and R Rowe (Berlin: Springer) p 341
   Harada Y, Masuda S and Ozaki H 1997 *Chem. Rev.* **97** 1897
   Nannarone S and Pasquali L 2001 *Nucl. Instrum. Methods* B **182** 227
   Krischok S, Höfft O and Kempter V 2002 *Nucl. Instrum. Methods* B **193** 466
[15] Bardi U and Rovida G 1983 *Surf. Sci.* **128** 145
[16] Rovida G and Pratesi F 1975 *Surf. Sci.* **51** 270
[17] Goddard P J and Lambert R M 1977 *Surf. Sci.* **67** 180
[18] Bowker M and Waugh K C 1980 *Surf. Sci.* **99** 639
[19] Plesanovas A, Castellani Tarabini A, Abbati I, Kaciulis S, Paolicelli G, Pasquali L, Ruocco A and Nannarone S 1992 *Surf. Sci.* **307–309** 890
[20] Pasquali L 1997 *PhD Thesis* University of Modena
   Ferro P, Moroni R, Salvietti M, Canepa M and Mattera L 1998 *Surf. Sci.* **407** 212
[21] Thermo VG 1999 UV source manual, Doc. N. HA03005, Issue 4 (11/99), England
[22] Staicu-Casagrande E M, Lacombe S, Guillemot L and Esaulov V A 2000 *Surf. Sci.* **407** L36
[23] Wu K, Wang D, Deng J, Wei X, Cao Y, Zei M, Zhai R and Guo X 1992 *Surf. Sci.* **264** 249
[24] Wu K, Wang D, Deng J, Wei X, Cao Y, Zei M, Zhai R and Guo X 1993 *Surf. Sci.* **285** L522
[25] Hagstrum H D 1954 *Phys. Rev.* **96** 336
   Hagstrum H D 1966 *Phys. Rev.* **150** 495
   Hood E, Boszo F and Metiu H 1985 *Surf. Sci.* **161** 491
[26] Sesselmann W, Woratschek B, Küppers J, Ertl G and Haberland H 1987 *Phys. Rev.* B **35** 8348
[27] Pasquali L, Nannarone S, Canepa M and Mattera L 1995 *Phys. Rev.* B **52** 17335
[28] Pasquali L, Sapet M C, Staicu-Casagrande E M, Cortona P, Esaulov V A, Nannarone S, Canepa M, Terreni S and Mattera L 2003 *Nucl. Instrum. Methods* B at press
[29] Canepa M, Cantini P, Mattera L, Terreni S and Valdenazzi F 1992 *Phys. Scr.* T **41** 226
[30] Canepa M, Guarniaschelli C, Mattera L, Polese M, Terreni S and Truffelli D 1991 *Rev. Sci. Instrum.* **62** 1431
[31] Bartels E and Goldmann A 1982 *Solid State Commun.* **44** 1419
[32] Kleinherbers K K, Janssen E, Goldmann A and Saalfeld H 1989 *Surf. Sci.* **215** 394
[33] Hufner S 1994 *Photoelectron Spectroscopy* (Berlin: Springer)
[34] Wei-Xue Li, Stampfl C and Scheffler M 2002 *Phys. Rev.* B **65** 075407
[35] Canepa M, Cantini P, Mattera L, Narducci E, Salvietti M and Terreni S 1991 *Surf. Sci.* **322** 271
[36] Lamble G M, Brooks R S, Ferrer S and King D A 1986 *Phys. Rev.* B **34** 2975
[37] Holmes D J, Panagiotides N, Dus R, Norma D, Lamble G M, Barnes C J, Della Valle F and King D A 1987 *J. Vac. Sci. Technol.* A **5** 703
[38] Endo O, Kondoh H, Yonamoto Y, Yokoyama T and Ohta T 2000 *Surf. Sci.* **463** 135
[39] Doll K and Harrison N M 2001 *Phys. Rev.* B **63** 165410
[40] Wang Y, Sun Q, Fan K and Deng J 2001 *Chem. Phys. Lett.* **334** 41