Coverage-Dependent Bond-Length Changes of Chlorine Adsorbed on Ag{110} Determined by Shadow-Cone-Enhanced Desorption

In a recent Letter by Lamble et al.,[1] it was concluded that when Cs, an electropositive metal, adsorbs on Ag{111} the Cs-Ag bond length increases significantly with increasing coverage while for Cl, an electronegative element, the adsorption on Ag{111} exhibits no change with coverage. In this Comment we demonstrate using an alternative technique, shadow-cone–enhanced desorption, that the Cl-Ag bond length does indeed change with coverage. In fact, the change for Cl adsorbed on Ag{110} is larger than that observed for Cs adsorbed on Ag{111}.[2,3]

Bond lengths for Cl on Ag{110} were determined using a shadow-cone–enhanced desorption methodology which has been described in detail.[2,3] The method has the advantage of high sensitivity to low coverages. If the shadow-cone shape is accurately known, the surface bond length may be readily determined from the angle associated with the maximum in the sputtering yield.

The measured bond lengths for Cl on Ag{110} after exposures to 0.15 to 3.8 L [1 L (langmuir) $= 10^{-6}$ Torr s] of Cl_2 are shown in Fig. 1. The results are obtained from data recorded under conditions similar to those shown in Fig. 2 of Ref. 2. The bond length was calculated from the angle of maximum Cl^- ion yield, corresponding to the intersection mechanism shown in the figure. With this scheme, it is assumed that the spacing between silver atom 1 and atom 2 is equal to the bulk spacing of 4.086 Å and that atoms 1 and 2 are the same distance below the surface plane. The Cl atom is placed in the fourfold bonding site as required by azimuthal angular anisotropies of the Cl^- ion.[3] The exposures associated with the observed LEED patterns are indicated in the figure. Only the bond lengths for the $p(2\times1)$ coverage and the higher $c(2\times4)$ coverage of 2.56 ± 0.04 Å are available from the surface extended x-ray-absorption fine-structure (SEXAFS) measurements.[4] These experiments are in agreement with our measurements in the high-coverage range, that is, a Cl-Ag bond length of 2.50 ± 0.06 Å.

Also shown in the figure is the variation of the chlorine $L_3M_{2,3}M_{2,3}$ Auger kinetic energy as a function of coverage. The spectral line shape undergoes a shape change and an energy shift which shows a direct correlation with the Cl bond-length change.[3] This is strong evidence that there is an associated change in the electronic structure of the valence states which is significant only at the low coverages below that used in the SEXAFS measurements. At the coverages studied with SEXAFS, the electronic factor remains constant.

In conclusion, our measurements confirm that there is a large decrease in bond length with increasing coverage of chlorine on Ag{110} from 2.90 to 2.50 Å. These results suggest from consideration of the magnitude of ionic radii that the bonding is ionic at low coverages, but is
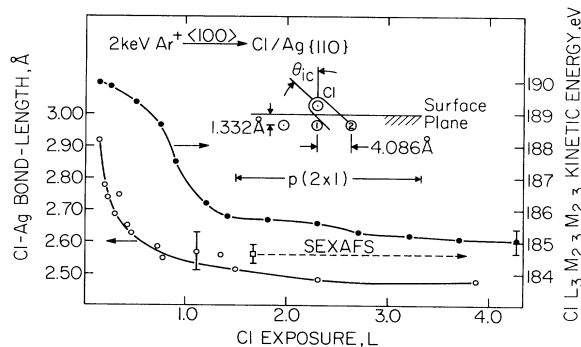

FIG. 1. Ag-Cl bond-length change (O) and Auger Cl L_3-$M_{2,3}M_{2,3}$ kinetic energy (●) as a function of Cl_2 exposure at 300 K. The reported value refers to the distance between the center of silver atom 1 and the Cl atom. The $p(2\times1)$ LEED pattern was observed in the exposure region as shown. The bond lengths from the SEXAFS experiments are associated with the LEED pattern; the same value was also obtained at a coverage beyond 4 L and associated with the $c(4\times2)$ LEED pattern (Ref. 5). Inset: The shadow-cone–induced desorption mechanism used to calculate the bond length is shown. The interplanar spacing refers to the relaxed clean-surface Ag{110} value. The shadow-cone shape was calculated using a Thomas-Fermi-Moliére potential with a scaling factor of 0.86.

forced into a more covalent configuration due to dipole-dipole interactions which are important as the number of surface charges increases. That is, the behavior is converse to the Cs-Ag situation, as expected from simple static Coulomb arguments. Moreover, our results are in good agreement with those from the SEXAFS method applied at higher coverages, confirming the covalent nature of the Ag—Cl bond.

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