

Coverage-dependent Bond Length of Chlorine Adsorbed on Cu{111}

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The adsorption of Cl₂ on Cu{111} at 300 K has been studied using shadow-cone-enhanced secondary ion mass spectrometry (SIMS). The system has been investigated for chlorine coverages ranging from 0.08 to 0.33 monolayer (ML), including the Cu{111}-($\sqrt{3} \times \sqrt{3}$)R30°-Cl surface. The secondary Cu⁺ ion intensity has been measured as a function of the incidence angle of the primary ion beam. The enhanced intensity features in the spectra are compared with results from a two-body interaction calculation that uses the Molière approximation to the Thomas-Fermi potential. A chlorine-copper interlayer spacing of 1.87 ± 0.04 Å is measured between the coverages of 0.17 and 0.33 ML. This value corresponds to a chlorine-copper bond length of 2.38 ± 0.04 Å. At 0.08 ML, the chlorine-copper bond length is expanded to 2.48 ± 0.04 Å. These results suggest that the chlorine-copper bond is more ionic in the low coverage limit.

INTRODUCTION

Adsorption onto metal surfaces is known to alter the bonding of atoms in the near-surface region. These adsorbate-induced changes are often manifested as an expansion or contraction of the surface and have previously been well documented.¹⁻⁷ Specifically, chlorine adsorption on copper is of industrial importance due to corrosion as well as its catalytic activity in reactions such as the production of dichloroethane from ethylene and HCl.⁸ Although extensive research has been performed on this system, little has focused on the chlorine-copper bond in the low coverage regime. In this paper, the coverage-dependent bonding of chlorine on Cu{111} in the coverage regime from 0.08 to 0.33 monolayer (ML) is discussed.

Our shadow-cone-enhanced secondary ion mass spectrometry (SIMS) results show that the chlorine-copper bond length contracts as chlorine coverage is increased. A bond length of 2.38 ± 0.04 Å is measured between the coverages of 0.17 and 0.33 ML, including the Cu{111}-($\sqrt{3} \times \sqrt{3}$)R30°-Cl surface. This result is in agreement with previous surface-extended x-ray absorption fine structure (SEXAFS) results.⁹ However, at a coverage of 0.08 ML, the chlorine-copper bond length is expanded to 2.48 ± 0.04 Å.

EXPERIMENTAL

A detailed description of the experimental arrangement can be found elsewhere.¹⁰ Briefly, the cryo-pumped ultrahigh vacuum chamber (2×10^{-10} Torr base pressure) is equipped with a stationary, differentially pumped PHI noble gas ion gun and electron optics for

low-energy electron diffraction (LEED). The detector is a Riber quadrupole mass filter equipped with a 90° electrostatic sector for energy selection of desorbed ions. This energy prefilter was used to collect those ions with kinetic energies of 6 ± 1 eV. The primary ion used in these experiments was 4.0 keV Xe⁺. The configuration of the set-up is shown in Fig. 1(a). The polar angle of incidence θ_i is defined with respect to the surface normal. The angle β is defined as the angle between the incident ion beam and the detector and was fixed at 40°. Using this configuration, the angular resolution is $\pm 0.5^\circ$ in the polar direction and $\pm 2^\circ$ in the azimuthal direction.

The Cu{111} crystal preparation included mechanical polishing to a mirror finish and was oriented to within $\pm 0.5^\circ$ by x-ray Laue diffraction. *In situ* preparation included repeated cycles of ion beam bombardment and annealing to 800 K. The presence of surface contaminants was monitored by SIMS and the quality of the surface structure was addressed using LEED. A variable leak valve controlled the amount Cl₂ (99.97%) introduced into the chamber. The temperature remained constant at 300 K during dosing. The Cu{111}-($\sqrt{3} \times \sqrt{3}$)R30°-Cl structure was prepared by dosing 3 L (1 L = 10^{-6} Torr · s) of Cl₂ while monitoring the LEED pattern.¹¹ Exposures were determined by an uncorrected pressure reading from a nude Bayard-Alpert ionization gauge. During SIMS experiments, an ion dose below the static limit ($< 10^{13}$ incident ions cm⁻²) ensured surface integrity.

RESULTS AND DISCUSSION

Shadow-cone-enhanced SIMS spectra are collected by varying the polar angle between the incident ions (keV) and the surface along a specific azimuth of the crystal. This technique has been applied in the characterization of many systems and is useful in determining bond

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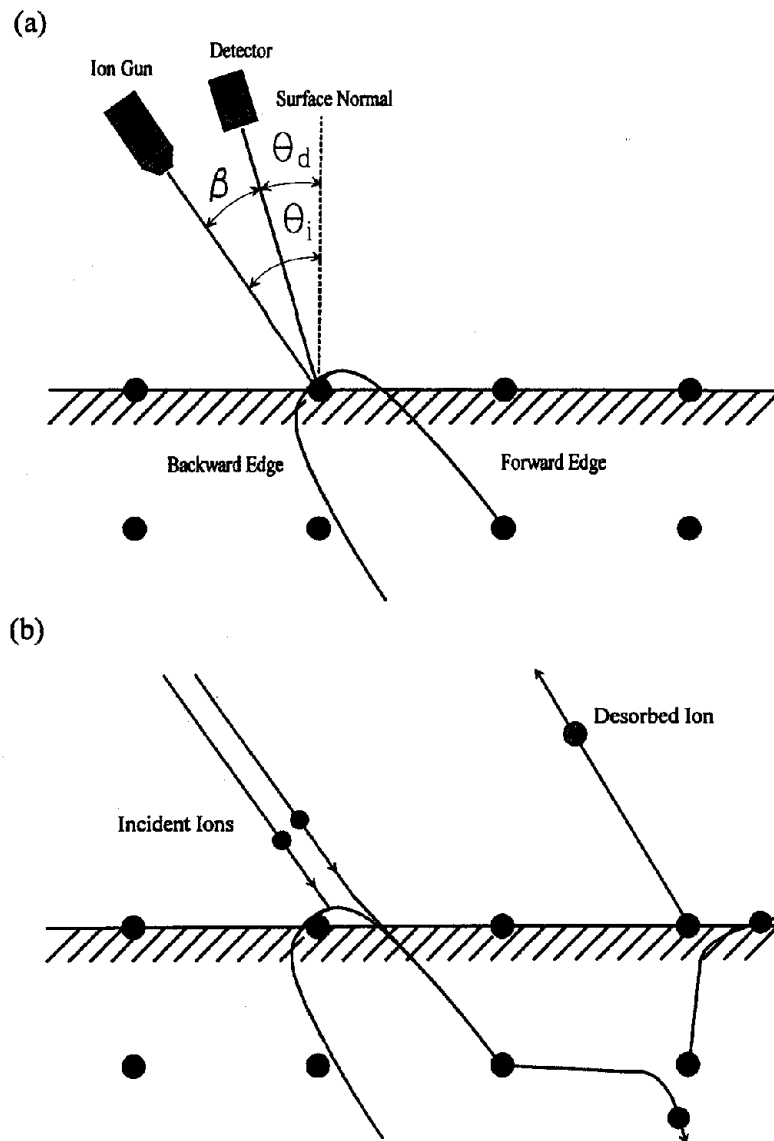


Figure 1. (a) Definition of the angles used in shadow-cone-enhanced SIMS experiments. A schematic of a shadow cone is illustrated, with the forward and backward edge designated as shown. (b) A schematic representation of a shadow cone, illustrating the relationship of shadow cones with desorbed particles.

lengths in the near-surface region.¹² A shadow cone is created by the nuclear-nuclear repulsion of the incident ions and a surface atom. At the edge of this shadow cone the incident flux is often enhanced by a factor of 5. The width of this high-flux region is $\sim 0.02 \text{ \AA}$.¹³ The increased desorbed ion yield in the shadow-cone-enhanced SIMS spectra is caused by direct interaction of the shadow cone edge with a nearby atom, which imparts momentum to the near-surface region. The collision cascade initiated by this momentum transfer results in enhanced desorption and gives rise to a peak in the detected ions. These peaks are utilized to interpret structure in the near-surface region by knowing the shape of the shadow cone created by the incident ions and the target atoms. The profile of the shadow cone for keV interactions can be approximated well by a two-body collision model that uses the Molière approximation to a Thomas-Fermi potential. This potential energy function requires knowledge of the Firsov screening factor for a given pair of colliding atoms. This factor depends on the atomic number of both atoms

and can be determined using an empirical relation¹⁴ of the form

$$f(Z_1, Z_2) = 0.54 + 0.045[(Z_1)^{1/2} + (Z_2)^{1/2}] \quad (1)$$

or by direct experimental measurement using a system with known bond lengths. Using Eqn (1), Firsov screening factors of 1.06 and 1.11 are determined for the Xe-Cl and Xe-Cu interactions, respectively.

Shadow cone peaks are denoted by the atom forming the shadow cone and the atom struck by the high-flux edge of the shadow cone. These atoms are designated by their positions in columns and rows. These labels are shown in Fig. 2. The letters F and B designate the forward and backward edges of the shadow cone, respectively. For instance, the mechanism F(1,1)(2,2) involves the forward edge of a shadow cone formed by atom (1,1) striking atom (2,2). A similar notation is used when the mechanism involves an adsorbed atom. Mechanism B(Cl,0)(1,1) involves the back edge of a shadow cone formed around a chlorine adatom striking atom (1,1).

+30° Azimuth

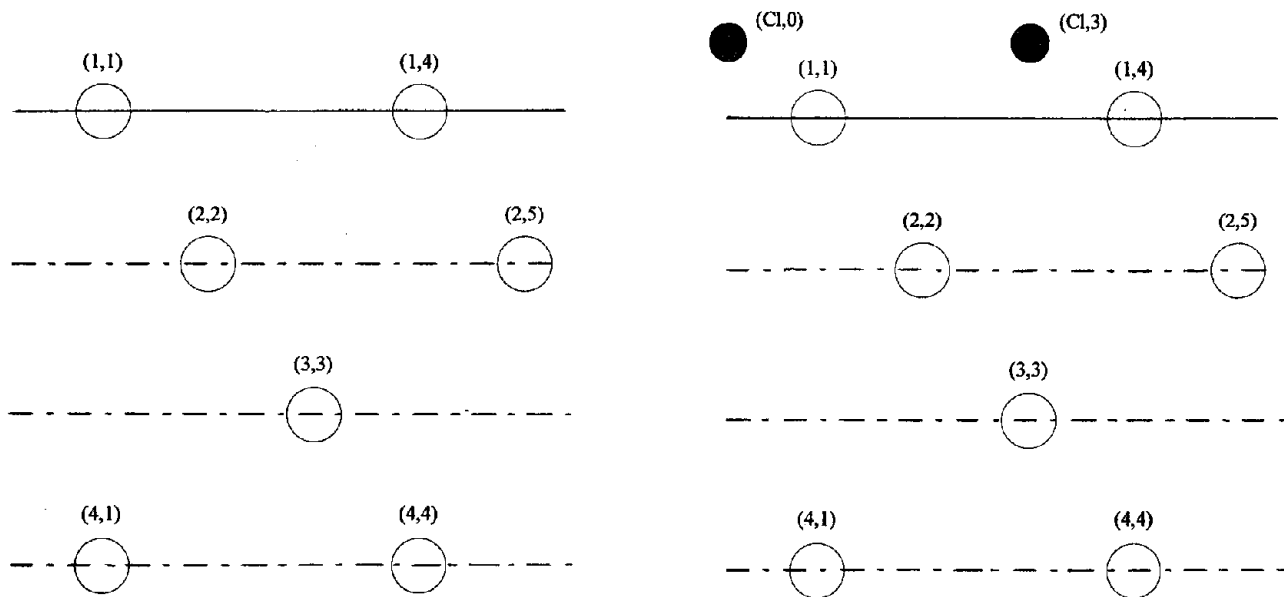


Figure 2. Schematic view of both the clean and chlorine-covered +30° azimuth. The atoms are designated by their positions in rows and columns. The gray circles represent chlorine atoms adsorbed in fcc sites.

A schematic of the top view of the Cu{111} surface along with azimuthal definitions is shown in Fig. 3. The three nonequivalent azimuths are labeled. The ±30° azimuths are distinguished by the location of the second and third layer atoms. Shadow-cone-enhanced SIMS experiments were performed along the +30° azimuth (Fig. 2). The +30° azimuth was chosen for experiments because the 0° azimuth has an interplanar separation of 0.74 Å while the 30° azimuths have an interplanar separation of 1.28 Å. This increased separation minimizes out-of-plane interactions, which should result in an increased signal-to-background ratio for the desired

interactions. Furthermore, according to our two-body collision model, interactions of interest should be better resolved along the +30° azimuth as compared to the -30° azimuth.

The desorbed secondary Cu⁺ intensity as a function of incidence angle of 4 keV Xe⁺ for clean Cu{111} is shown in Fig. 4. A representative feature for the clean, unreconstructed Cu{111} surface occurs at an incidence angle of 70°. The feature is a result of increased desorption and is commensurate with the high-flux edge of the shadow cone aligning with a neighboring first-layer atom [F(1,1)(1,4)]. This peak is used to determine the Firsov screening length factor, because no lateral reconstruction has been measured previously.¹⁵ This experimental calibration confirms the Firsov screening length factor calculated using Eqn (1).

Shadow-cone-enhanced SIMS spectra for Cl on Cu{111} at various coverages are shown in Fig. 4. The Cu{111}-($\sqrt{3} \times \sqrt{3}$)R30°-Cl surface is produced after exposing 3 L of Cl₂ at room temperature. Exposures of 0.75 and 1.5 L are equivalent to coverages of 0.08 and 0.17 ML, respectively. This assumes that the initial sticking coefficient is constant. One would expect that as chlorine is adsorbed onto the Cu{111} surface the F(1,1)(1,4) should fade because fewer Cu atoms are exposed at the surface. The F(1,1)(1,4) mechanism disappears as a function of increased exposure to Cl₂, and is further evidence for the assignment of F(1,1)(1,4).

As the chlorine coverage is increased it becomes possible to use shadow cone mechanisms involving the Cl adatoms to address the bonding of these species to the surface. Photoelectron diffraction studies⁹ along with our angle-resolved SIMS results¹⁶ show that chlorine adsorbed on the Cu{111} surface occupies the threefold hollow above a third-layer atom (fcc site) in this coverage regime. One interaction that would be expected in the Cl overlayer is the F(Cl,0)(Cl,3) interaction. This

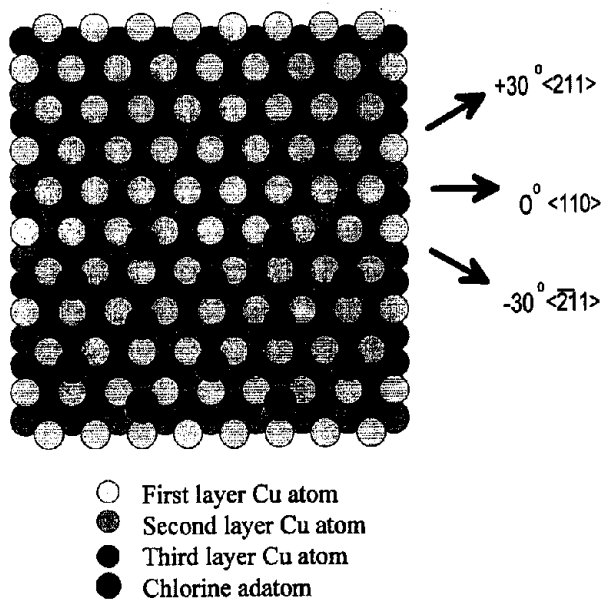


Figure 3. (Top) A schematic of the Cu{111} surface. (Bottom) A schematic of the ($\sqrt{3} \times \sqrt{3}$)R30° Cl/Cu{111} model surface.

Table 1. Comparison of coverage-dependent bond length measurements for halogen adsorption onto clean metal surfaces

	Bond length Å	Δ Bond length Å	Coverage	Technique	Reference
I/Rh{111}	2.71 \pm 0.06	none	0.1–0.33	ATLEED	19
Cl/Ag{111}	2.70 \pm 0.01	none	0.33–0.66	SEXAFS	17
I/Ni{100}	2.78 \pm 0.02	none	0.125–0.5	SEXAFS	18
Cl/Ag{110}	2.50–2.90 \pm 0.06	0.4	0.05–0.5	SIMS	20
Cl/Cu{111}	2.39–2.49 \pm 0.04	0.1	0.1–0.5	SIMS	present

interaction is predicted to occur at $\theta_i = 74.5^\circ$ for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ coverage. As shown in Fig. 4, there is a shoulder at 74.5° associated with this interaction, although the intensity is low. Energy transfer into the surface region as a result of this interaction is relatively inefficient, resulting in this behavior. Other shadow cone interactions, however, such as the $B(\text{Cl},0)(1,1)$, should involve relatively more momentum transfer into the near-surface region. Thus, they have higher intensities and can be monitored as a function of coverage, revealing changes in the Cu–Cl bond length.

Although the shadow-cone-enhanced SIMS spectra shown in Fig. 4 are rich with structure, we will only consider mechanisms that involve two atoms. There are, however, more complex shadow cone mechanisms that involve more than two atoms. These multi-atom mechanisms are difficult to predict and evaluate due to the extensive calculations necessary. Software to predict these mechanisms is being developed by our group and will be discussed in a future publication.

We chose to monitor the $B(\text{Cl},0)(1,1)$ interaction as a function of coverage. This interaction is clearly seen in

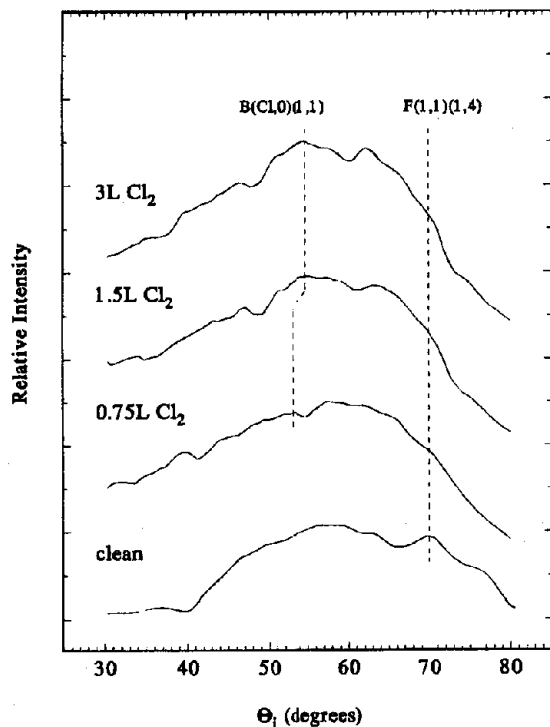


Figure 4. The relative intensity of Cu^+ ions desorbed from clean $\text{Cu}\{111\}$ and three different coverages of chlorine plotted as a function of the ion beam incident angle. The ion beam is parallel to the $+30^\circ$ azimuth. The dashed lines indicate angles calculated from results of the two-body collision model described in the text.

the $\text{Cu}\{111\}$ – $(\sqrt{3} \times \sqrt{3})R30^\circ$ –Cl surface at an incidence angle of 54.7° . The interlayer spacing between chlorine and copper is calculated to be 1.87 ± 0.04 Å, assuming no lateral displacement of the first-layer copper atoms. This interlayer spacing is in excellent agreement with previous SEXAFS studies⁹ and yields a Cu–Cl bond length of 2.38 ± 0.04 Å. The $B(\text{Cl},0)(1,1)$ interaction is also detected at $\theta_i = 54.7^\circ$ in the 1.5 L exposed surface, confirming that the interlayer spacing is 1.87 ± 0.04 Å at this coverage. The $B(\text{Cl},0)(1,1)$ interaction shifts to $\theta_i = 53.0^\circ$ in the 0.75 L exposed surface. This change in angle represents expansion of the Cu–Cl bond to 2.48 ± 0.04 Å, suggesting that the Cl–Cu bond is more ionic compared to the higher coverages. Continued investigation to lower coverages is of interest but is not feasible because the $B(\text{Cl},0)(1,1)$ signal becomes masked by the background. This is as expected because fewer chlorine adatoms are present.

The coverage-dependent bond length of halogens on metal surfaces has been in debate for more than a decade. At least four previous coverage-dependent bond length experiments have been reported involving halogens on metal surfaces.^{17–20} One of the previous studies detected a coverage-dependent bond length.²⁰ Summarized in Table 1 are the five experimental results. We contend that the observation of no bond length change in the $\text{Cl}/\text{Ag}\{111\}$, $\text{I}/\text{Ni}\{100\}$ and $\text{I}/\text{Rh}\{111\}$ experiments is in part due to the presence of adsorbate–adsorbate interactions. This will be the subject of a work of further detail.²¹

CONCLUSIONS

We have presented experimental evidence showing that the Cu–Cl bond length varies as a function of coverage. At a critical coverage of ~ 0.1 ML the Cl–Cu bond length expands from 2.38 to 2.48 ± 0.04 Å. This conclusion is in agreement with previous calculations that predict a charge transfer between chlorine and a metal substrate.²²

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