

STM Observation of Pt{111}(3×3)-Cl and c(4×2)-Cl Structures

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The adsorption of chlorine on a Pt(111) surface at 90 K has been studied using scanning tunneling microscopy (STM) in ultra-high vacuum environments. The adsorbed chlorine atoms give rise to two different ordered structures, (3×3)-Cl and c(4×2)-Cl, depending on the coverage. It has been determined from the STM image that the absolute coverage of (3×3)-Cl structure is 0.44, which is not in agreement with coverage calibrated by a low energy electron diffraction technique together with an Auger electron spectrometer and a thermal desorption spectrometer. The Cl atoms bound to on-top sites at the Pt(111)(3×3)-Cl surface appeared to effectively perturb the density of states of Pt atoms, as compared with that bound to bridging sites. The other ordered structure, c(4×2)-Cl, with small domain sizes, consists of both on-top and bridge-bonded species with a saturation coverage of 0.5.

Keywords : STM, Platinum, Chlorine.

Introduction

The interaction of halogens (or halides) with metal surfaces has received considerable attention in surface chemistry because of its relevance to poisoning of adsorption sites, surface corrosion, etching and heterogeneous catalysis, as well as for fundamental aspects.¹ Particularly, since the halogens iodine (or iodide) and bromine (or bromide), so-called specific adsorption species, can be strongly bound to metal surfaces, the adsorption of these two species on Pt(111) surfaces has been studied extensively in an ultra-high vacuum (UHV), in air and under in-situ environments.²⁻⁹ Briefly, in the case of the adsorption of iodine, three structures, ($\sqrt{3} \times \sqrt{3}$) R30° ($\theta = 0.33$), ($\sqrt{7} \times \sqrt{7}$) R19.1° ($\theta = 0.43$) and (3 × 3) structures ($\theta = 0.44$), were investigated by means of structural probes, such as scanning tunneling microscopy (STM), surface x-ray scattering (SXS) and low energy electron diffraction (LEED).²⁻⁷ Adsorption of bromine led to the formation of (3 × 3) ($\theta = 0.44$) and (7 × 7) ($\theta = 0.51$) structures with a higher maximum coverage.^{2,8,9} These results are summarized in Table 1. On the other hand, chlorine (or chloride), having a relatively weak strength of interaction, was adsorbed on a Pt(111) electrode over coverage ranges between 0.4 and 0.6, but did not form any ordered structure with long-range order under in-situ environments.² In UHV environments, however, a sharp (3 × 3) LEED pattern was reported to appear just below the maximum coverage, and then change into a diffuse pattern with a high background intensity at saturation coverage.¹⁰⁻¹³ Coverage of the (3 × 3) structure of Cl having any multiple of 1/9 was suggested to be 2/9,¹⁰ 1/3^{11,12} or 0.51 ± 0.06 ,¹³ which was thoroughly calibrated by thermal desorption spectroscopy (TDS) and Auger electron spectroscopy (AES). Unfortunately, however, the value of absolute coverage proposed for the Pt(111)(3 × 3)-Cl structure is controversial. No other ordered structure has been reported.

Diffraction techniques, such as LEED and SXS, used to observe periodic structures of adlayer are frequently required for any ordered structure with long-range order.^{2,14} STM has been used extensively to determine the detailed structure of adlayers chemisorbed on metal surfaces with atomic resolution, although adsorbed molecules are sometimes distorted or even invisible in STM images.¹⁵ However, to our knowledge, there has been no previous structural study of Cl on Pt(111) by STM under UHV circumstances. In this article, we describe STM observation of the ordered structures of Cl adlayer on a Pt(111) surface after exposure to HCl gas under UHV environments.

Experimental Section

The apparatus and the sample preparation procedure have been described previously.^{14,16} The experiments were carried out in a UHV chamber with a base pressure of 1×10^{-8} Pa. The system was equipped with a reflection high-energy electron diffractometer (RHEED), a quadrupole mass spectrometer, a variable leak valve and STM (JEOL, JSTM-4610) in the STM observation chamber, as well as an Ar⁺ ion sputtering gun and an O₂ gas variable leak valve in the sample treat chamber. All STM images presented here were obtained in a constant height mode, using tungsten tips. The tip was prepared by electrochemical etching of a tungsten wire with a diameter of 3 mm at 10 V dc in a 2 M NaOH solution and cleaned by heating in a vacuum and by field evaporation while tunneling. The bias voltage was referred to the sample voltage with respect to the tip. The temperature of a sample in the STM chamber was measured with a semiconductor-diode sensor close to but not in direct contact with the sample.

A single crystal Pt(111) sample was oriented to within 1° accuracy by using the Laue X-ray method and was polished using conventional metallographic technique. It measured

Table 1. Change of ordered structures for halogens (I, Br and Cl) adsorbed on a Pt(111) surface as a function of coverage in a UHV and under in-situ environments

Halogen	In situ		UHV	
	Structure	Coverage	Structure	Coverage
I ²⁻⁷	($\sqrt{7} \times \sqrt{7}$)R19.1° (3 × 3)	0.43 0.44	($\sqrt{3} \times \sqrt{3}$)R30° ($\sqrt{7} \times \sqrt{7}$)R19.1°	0.33 0.43
Br ^{2,8,9}	(3 × 3) (7 × 7)	0.44 0.51	(3 × 3)	0.44
Cl ¹⁰⁻¹³		0.4-0.6	(3 × 3)	0.22, 0.33, 0.45-0.57

approximately 5 mm × 5 mm × 1 mm and was mounted by spotwelding with two Pt wires parallel to each other. The sample was heated with an electron beam heater and cooled to 90 K by filling the cryostat with liquid nitrogen. The Pt sample was cleaned by repeated cycles of Ar⁺ ion sputtering, annealing in the presence of oxygen of 2 × 10⁻⁵ Pa and flashing for 60 sec. The cleanliness and order of the surface were checked by RHEED and STM. Hydrogen chloride gas was introduced into the chamber by a gas-pulsed doser. A stainless steel manifold behind the gas doser was rinsed with fresh HCl gas to minimize contamination before exposing the sample to HCl.

Results and Discussion

A large, clean Pt(111)-(1 × 1) surface (more than 50 × 50 nm² in size) free of steps was observed before introducing hydrogen chloride molecules. After exposing the clean (111) surface to a low dose of HCl gas (corresponding to *ca.* 1.5 L) at 90 K, an STM image of adspecies adsorbed on the Pt(111) surface was obtained as shown in Figure 1(a). An ordered layer associated with the adsorbates was consistently observed over wide surface regions. There are no steps in the substrate except for domain boundaries of adsorbates in the STM image. Figure 1(b) shows an expanded, filtered STM image of Figure 1(a). It is clearly seen that the image contains two types of spots, bright spots and darker ones, which correspond to high and lower tunneling currents, respectively. From the image of Figure 1(b) the distance between the bright spots was measured to be about 3a, where a is (1 × 1) surface lattice parameter (2.78 Å). Darker spots are centrally located between the bright spots. A hexagonal structure formed by the bright spots is completely parallel to the directions of the three close-packed atomic rows of the underlying Pt(111)-(1 × 1) lattice. Considering the distance between spots and the orientation between the adlayer and the substrate, the observed structure can be classified as a (3 × 3) structure.

The adsorption of halogens on metal surfaces has been studied extensively in UHV and under in-situ environments.^{1-9,17-19} Metal halide compound is reported to be formed by halogens adsorption on substrate surfaces, such as Cu, Ag and Au^{17,18} (so-called surface-enhanced Raman scattering-active metals), as well as the most open Ni(110)¹⁹ sur-

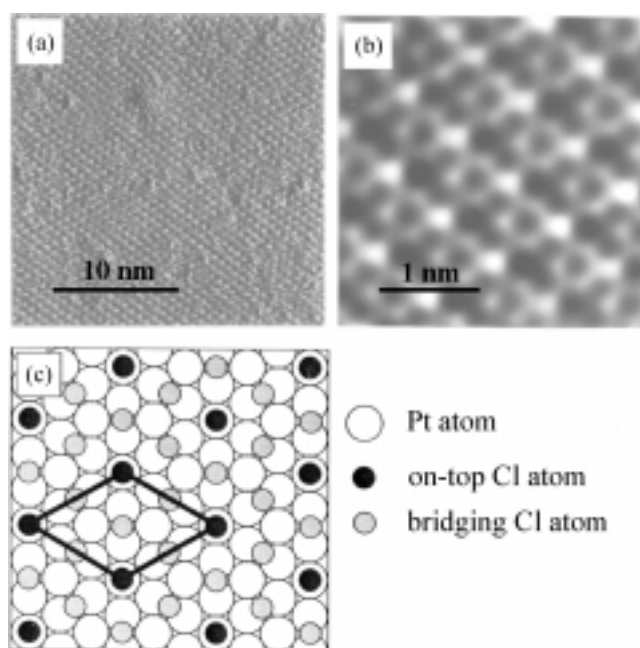


Figure 1. (a) STM image, over a wide region (25 × 25 nm²), of chlorine (or chloride) chemisorbed on a clean Pt(111) surface after an exposure of a small amount of HCl exposure (*ca.* 1.5 L) at 90 K. (b) Expanded STM image (3.1 × 3.1 nm²) of Figure 1(a). (c) Structural model of Pt(111)(3 × 3)-Cl with a coverage of 0.44. Pt atoms are shown as large open circles, smaller solid and shaded circles indicate Cl atoms bound to on-top and bridging sites, respectively. Tunneling conditions: sample bias voltage = 0.462 V and tunneling current = 1.07 nA.

face of the low index surfaces for fcc metals. However, adsorption of I, Br or Cl on a Pt(111) surface did not induce surface reconstruction or compound formation with substrate atoms.²⁻¹³ A system of HCl/Pt(111) was investigated by Wagner and Moylan, using LEED, TDS and HREELS.¹⁰ The result showed that HCl molecules were dissociated on a Pt(111) surface during adsorption because the H-Cl stretching mode was not detectable through impact scattering in HREELS. An equivalent (3 × 3) LEED pattern was observed after exposing Cl₂ or HCl on Pt(111).¹⁰⁻¹² Accordingly, they concluded that Pt-Cl interactions are sufficiently strong to establish the surface periodicity and hydrogen goes along for a structural ride on the basis of the same LEED pattern observation.¹⁰ Therefore, the spots observed in our STM image are interpreted as the Cl atoms rather than the substrate Pt atoms or the dissociated H atoms. A corresponding structural model for the (3 × 3) structure is shown in Figure 1(c). Pt atoms are shown as large open circles, smaller solid and shaded circles indicate adsorbates bound to on-top and bridging sites, respectively. The on-top Cl atom is imaged as a bright spot because of its long vertical distance from the surface. As a result, the darker and bright spots are assignable to the bridging and on-top adspecies, respectively. Since the unit cell of the (3 × 3) structure contains one on-top and three bridging adsorbates, a coverage of the overlayer is estimated to be 4/9. Such a (3 × 3) structure with a coverage of 0.44 is identical to structures proposed for the Pt(111)(3 × 3)-I²⁻⁷

and Pt(111)(3 × 3)-Br.^{2,8,9}

A (3 × 3) LEED pattern, with the sharpest intensity, from adsorbed Cl atoms on a Pt(111) surface reportedly has been observed at a coverage of 2/9,¹⁰ 1/3^{11,12} or 0.51 ± 0.06 .¹³ The values of the three coverages were calibrated on the basis of LEED with the aid of AES signal and thermal desorption peak area. For comparison, an ordered layer of iodine or bromine with an equivalent (3 × 3) structure had a coverage of 4/9,²⁻⁹ higher than 2/9¹⁰ or 1/3.^{11,12} For the case of adsorption of Cl with a smaller radius, therefore, a coverage of either 2/9 or 1/3 is a small possibility. The value of 0.51 ± 0.06 ¹³ has no exact multiple of 1/9. Consequently, the absolute coverage should be determined directly from the atomically resolved STM image. There are some small discrepancies between calibrated and absolute coverages.¹⁶

Figure 2(a) shows an STM image taken for the same (3 × 3)-Cl surface used in Figure 1 but under different tunneling conditions, such as high tunnel current (2.04 nA) and very small bias voltage (0.015 V). The nearest-neighbor spot distance is equal to the length of a Pt(111)-(1 × 1) surface unit cell. The three directions of a hexagonal structure in the image are completely parallel to those of the three close-packed atomic rows of the (1 × 1) lattice. Therefore, the spots appear to be due to the underlying Pt atoms. It is well known that substrate metal surfaces are sometimes visible under tunneling conditions such as both a higher tunneling current and a sample bias voltage near the Fermi level.¹⁴ Two kinds of Pt atoms with bright and dark spots are clearly observed in the image. The spots in the three directions (indicated as arrows) are brighter than others. To explain the presence of the two spots, we must consider an effect of Cl adsorption on the substrate Pt atoms since a Pt surface rearrangement was not induced by Cl adsorption as mentioned above.¹⁰⁻¹² Figure 2(b) shows three types of Pt atoms, depending on the sites of the adsorbed Cl atoms. Bare Pt atoms are shown as open circles, solid and shaded circles indicate Pt atoms bound to on-top and bridging Cl atoms, respectively. The ratio of the three spots is 1 : 6 : 2. Compar-

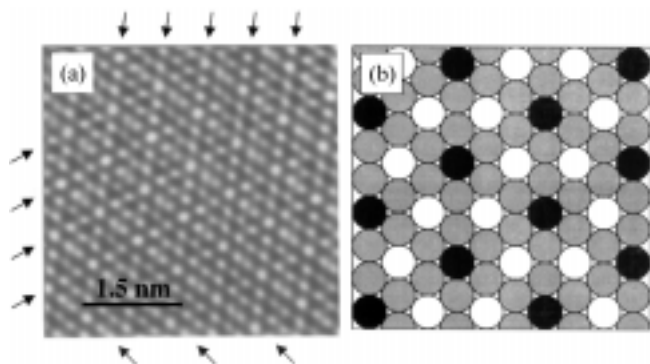


Figure 2. (a) STM image ($4.4 \times 4.4 \text{ nm}^2$) taken for the same, Cl-covered surface used in Figure 1(a) but under different tunneling conditions. Tunneling conditions: sample bias voltage = 0.015 V and tunneling current = 2.04 nA. (b) Pt(111)(3 × 3)-Pt structure consisting of three types of platinum atoms. Bare Pt atoms are shown as open circles, solid and shaded circles indicate Pt atoms bound to on-top and bridging Cl atoms, respectively.

ing the image 2(a) with the Figure 2(b), it is probably found that bright spots are assignable to Pt atoms bound to on-top Cl atoms, and dark spots are assignable to the bridging Cl-bound Pt atoms and the bare Pt atoms. The result is qualitatively explained as charge transfer from substrates. Work function was reported to increase at a coverage appearing a (3 × 3) LEED pattern because adsorbed Cl atoms act as electron acceptors.^{11,12} Assuming that the capacities of adsorbed chlorine atoms for accepting charge are constant irrespective of the adsorption site, the amount of charge transfer per substrate Pt atom decreases as the coordination number of Cl adsorbate atoms increases.²⁰ Electronic charge density near the Fermi level decreases on Pt atoms bound to on-top Cl atoms, while electronic charge density on the bridging Cl-bound Pt atoms remains nearly unchanged and becomes similar to that on the bare Pt atoms. As a result, we speculate that the Cl atoms on-top sites relatively perturb the density of states of the underlying Pt atoms.

Figures 3(a) and 3(b) show STM images obtained after HCl exposure was increased to approximately 2 L (saturation coverage) with different image size. The domain size of periodic structures is small as indicated in the image 3(a). Three ordered structures, associated with the adsorbed Cl atoms, rotated $\pm 120^\circ$ with respect to each other are clearly seen in Figure 3(a). A magnified STM image (Figure 3(b)) contains a darker spot (positioned at the center of a rectangle consisting of four bright spots) and a bright one. The number of bright spots is equal to the number of darker spots. From the distances between spots, the adsorbed Cl atoms have a

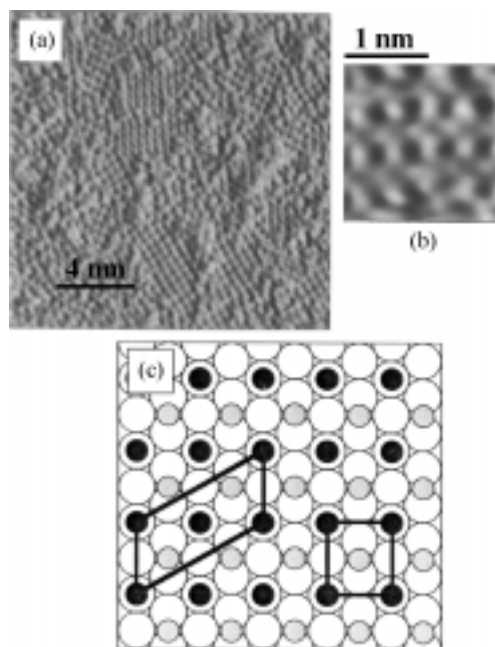


Figure 3. (a) STM image of chlorine adsorbed on the Pt(111) surface at a saturation coverage of HCl gas ($16.4 \times 16.4 \text{ nm}^2$). (b) High-resolution STM image ($1.88 \times 1.88 \text{ nm}^2$) of 3(a). (c) Structural model of Pt(111)-c(4 × 2)-Cl (or $(\sqrt{3} \times 2)\text{rect}$ structure) with a coverage of 0.5. Tunneling conditions for (a) and (b): sample bias voltage = 0.368 and 1.859 V, and tunneling current = 1.62 and 0.73 nA, respectively.

$c(4 \times 2)$ structure (or $(\sqrt{3} \times 2)$ rect structure in the rectangular notation) with a coverage of 0.5. The $c(4 \times 2)$ structure is identical to a $c(4 \times 2)$ structure previously reported for CO/Pt(111) system.¹⁴ From a detailed discussion for a variety of $c(4 \times 2)$ structures corresponding to a coverage of 0.5,²¹ the bright and darker spots are assignable to the Cl atoms adsorbed at on-top and bridging sites, respectively. Figure 3(c) exhibits a corresponding structural model for the $c(4 \times 2)$ structure formed by the adsorbed Cl atoms. No LEED patterns from a Cl/Pt(111) system have previously been detected at a saturation coverage.¹⁰⁻¹³ On the contrary, our STM image showed that the adsorbed Cl atoms give rise to a very small $c(4 \times 2)$ domain. The discrepancy between LEED and STM is sometimes due to the domain size of ordered overlayer.¹⁴

Saturation coverage of iodine and bromine on a Pt(111) surface were reported to be 0.44²⁻⁷ and 0.51,^{2,8,9} respectively, as indicated in Table 1. The two values are very close to the 0.41 and 0.51 deduced for hexagonal close packings of their species with the Van der Waals radii of 2.16 and 1.95 Å, respectively.²² For chlorine adsorption a saturation coverage (the Van der Waals radius=1.81 Å²²) should be around 0.59. The small difference (0.09) in coverage between $c(4 \times 2)$ structure and hexagonal close packing is easily explained on the basis of higher local coverage. There are many disordered regions as shown in Figure 3(a). An adspecies density between domain boundaries is higher than that inside ordered domains. However, a (3×3) LEED pattern from the adsorbed Cl atoms on a Pt(111) surface has been reported to be always observed over 70-90 percent of the maximum coverage.¹⁰⁻¹³ Our relative coverage ratio of (3×3) to $c(4 \times 2)$ structures is 0.88, lying in the range of the known values.¹⁰⁻¹³

Finally, we discuss the origin of the surface phase transition of (3×3) to $c(4 \times 2)$ structures with increasing coverage of the adsorbed Cl atoms. In the case of (3×3) structure, the coverage ratio of Cl atoms adsorbed at on-top to bridging sites is 0.33, increasing to 1 when the total coverage was increased to 0.5. That is, Cl atoms bonded to the bridging sites were indicated to migrate to on-top sites with increasing Cl coverage. Such a site conversion can be explained by the difference in surface area occupied by Cl atoms. The surface area of Cl at bridging sites is two times as large as that at on-top sites. Therefore, at a high coverage of 0.5 corresponding to the $c(4 \times 2)$ structure, it was favorable that adsorbed Cl atoms migrate to on-top sites.

Conclusion

Scanning tunneling microscopy was used to determine detailed atomic structures of the chemisorbed chlorine (or chloride) adlayer on a Pt(111) surface at 90 K in ultra-high vacuum circumstances. Two ordered structures, (3×3) -Cl

and $c(4 \times 2)$ -Cl, were formed during HCl exposure. The absolute coverage of (3×3) -Cl structure, which contains one on-top and three bridging species, was 0.44. The underlying Pt atoms at the Cl-covered Pt surface were visible under tunneling conditions such as higher tunneling current and sample bias voltage near the Fermi level. The Cl atoms bound to on-top sites were found to effectively perturb the density of states of Pt atoms, as compared with those bound to bridging sites. The other ordered structure, $c(4 \times 2)$ -Cl, consisted of both on-top and bridge-bonded species with a saturation coverage of 0.5.

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