Chlorine adsorption on Cu{111}: low-temperature adsorption, electron-stimulated desorption and chloride formation

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Abstract. Chlorine adsorption on Cu{111} has been studied at low temperatures using LEED and AES. At 165 K a $(6\sqrt{3} \times 6\sqrt{3})R30°$ chemisorbed structure was formed at saturation. At 110 K adsorption continued, forming multilayers of copper chloride with the $(6\sqrt{3} \times 6\sqrt{3})R30°$ structure still intact at the interface between the chloride and the copper. Electron-stimulated desorption was observed from the $(6\sqrt{3} \times 6\sqrt{3})R30°$ structure at 165 K but not at 300 K, which is consistent with a high surface mobility for chemisorbed chlorine.

This work forms part of a larger study of the cupric-chloride-catalysed oxychlorination reaction. Chlorine adsorption on Cu{111} at 300 K has been studied [1] and exhibits a $(\sqrt{3} \times \sqrt{3})R30°$ structure at $\frac{1}{3}$ML coverage in which the chlorine atoms are adsorbed in the 'FCC'-type three-fold hollows [2]. For higher coverages a compressive phase is observed [1, 3] which saturates at 0.45 ML in a coincident $(6\sqrt{3} \times 6\sqrt{3})R30°$ structure.

Chlorine was either generated in vacuum using a solid-state electrochemical cell [4] or admitted via a leak valve and dosing tube from the bulk gas. Electron-stimulated desorption was unobservable under the LEED beam ($\simeq 115$ eV, $\simeq 15$ A m^{-2}) but pronounced under the incident beam used for AES (2 keV, $\simeq 125$ A m^{-2}). The chlorine 181 eV and copper 60 eV and 920 eV Auger peaks were used to monitor adsorption and desorption. To avoid ESD specifically, a defocused incident beam ($\simeq 3$ A m^{-2}) was used for AES.

Adsorption at 100 K proceeded via the same sequence of structures $((\sqrt{3} \times \sqrt{3})R30° \rightarrow \text{compression} \rightarrow (6\sqrt{3} \times 6\sqrt{3})R30°)$ as for room-temperature adsorption to monolayer coverage. Adsorption then continued with the formation of multilayers of a copper chloride characterised by saturation of the chlorine Auger peak and constant but reduced values for the copper Auger peaks, after a dose equivalent to about 6 ML of chlorine. LEED observations showed that the $(6\sqrt{3} \times 6\sqrt{3})R30°$ structure remained intact at the interface of the copper and the copper chloride, as the diffraction pattern remained sharp until it became submerged in the rising background due to the chloride layer. This implies that copper can diffuse through the chemisorbed layer, to form the chloride, without destroying its structure. To allow this the chemisorbed layer must be capable of distortion, to allow passage of the copper ion, followed by a healing process, which reforms the structure. This is consistent with the compressional nature

of the $(6\sqrt{3} \times 6\sqrt{3})R30°$ structure [1, 3] and the mobility of surface chlorine, as shown below.

Electron-stimulated desorption from the $(6\sqrt{3} \times 6\sqrt{3})R30°$ structure was not observable by AES (125 A m^{-2}) at 310 K, but was pronounced at 165 K. The 181 eV chlorine Auger peak underwent an initial exponential decay with respect to time for a constant incident electron flux (125 A m^{-2}); the rate then decreased to zero at a small, but finite chlorine coverage. As the initial rate of ESD was proportional to the current density, the desorption rate could be reduced to negligible proportions by defocusing the incident beam to 3 A m^{-2} as described above. These results are consistent with a model in which adsorbed chlorine is capable of diffusing rapidly at 310 K over distances of the order of hundreds of μm, so as to replenish an area that is being depleted by ESD. However, at 165 K the diffusion rate is greatly reduced, and ESD becomes observable as a reduction in coverage under the electron beam used for AES.

The surface structures and general behaviour of chlorine on Cu{111} are remarkably similar to those of chlorine on Ag{111} ([5]; for a review, see [6]) and indeed the halides of both metals exhibit remarkable solid-state properties. The precise nature of the copper chloride formed at low temperatures requires further elucidation, as does its formation mechanism. For chlorine adsorption on polycrystalline copper at 210 K, a mixed layer of copper chloride and molecular chlorine has been reported [7]. However, by analogy with the silver adsorption system, it is possible that surface chlorine may be capable of dissolving into the bulk of the copper crystal, thus explaining the lack of surface chloride at room temperature.

Acknowledgments

References

[1] Goddard P J and Lambert R M 1977 *Surf. Sci.* **67** 180
[2] Crapper M D, Riley C E, Sweeney P J J, McConville C F, Woodruff D P and Jones R G 1987 *Surf. Sci.*
   182 213
[3] Walter W K and Jones R G 1989 in preparation
[4] Spencer N D, Goddard P J, Davies P W, Kitson M, Lambert R M 1983 *J. Vac. Sci. Technol.* A **1** 1554
[5] Bowker M and Waugh K C 1983 *Surf. Sci.* **134** 639
[6] Jones J G 1988 *Prog. Surf. Sci.* **27** 5
[7] Park S, Rhodin T N and Rathbun L C 1986 *J. Vac. Sci. Technol.* A **4** 168