

## Adsorption of halogens on metal surfaces

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### ABSTRACT

This paper presents a review of the experimental and theoretical investigations of halogen interaction with metal surfaces. The emphasis was placed on the recent measurements performed with a scanning tunneling microscope in combination with density functional theory calculations. The surface structures formed on metal surface after halogen interaction are classified into three groups: chemisorbed monolayer, surface halide, bulk-like halide. Formation of monolayer structures is described in terms of surface phase transitions. Surface halide phases are considered to be intermediates between chemisorbed halogen and bulk halide. The modern theoretical approaches in studying the dynamics of metal halogenation reactions are also presented.

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### 1. Introduction

Halogens form a particular group in the periodic table. Due to their extremely high electronegativity, halogens can form chemical compounds with all metals and most nonmetals. In this connection, one can expect significant changes in atomic arrangement and electronic structure of surfaces when covered with halogen atoms.

The first attempts to understand halogen interaction with metals and semiconductors were related to the importance of this process in industry, first of all in heterogeneous catalysis and microelectronics [1,2]. In heterogeneous catalysis, halogens are widely used to modify properties of transition metal catalysts. The most striking example is ethylene epoxidation in the presence of silver catalyst - one of the most important industrial chemical reactions [3]. Addition of small amount of chlorine to the surface of silver catalyst significantly improves its selectivity towards ethylene epoxidation. Though this positive effect of chlorine has been known

for already 120 years and is widely used in industry, its origin is not yet clear. Many scientists believe that the surface science studies of this catalytic reaction in well-defined UHV conditions on single crystal surfaces could elucidate some key processes that are impossible to study “in vivo” in the conditions of a real chemical reactor [4].

As knowledge about halogen adsorption on crystal surfaces accumulated, it became clear that these systems are of interest not only from practical but also fundamental point of view. Halogens are ideal elements for the study of general trends in the interaction of active gases with solids [1,2]. Compared to another active gas, oxygen, halogens have several advantages. First, their sticking coefficient to the surface is a few orders of magnitude greater than that of oxygen, and is usually close to unity [2]. This makes halogens very handy for UHV conditions, where low pressure of gases is required. Second, an oxide film is usually very stable and hard to remove from the surface. In contrast, halogen monolayers (or thin halide films) can be easily removed by heating the surface to moderate temperatures (400–700 °C) [2].

Halogens on metals are typical electrochemical systems since they constitute one of the simplest models for specific adsorption. In this connection, halogens on metal surfaces have been actively

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studied not only in ultrahigh vacuum but also in the electrochemical environment. In this review, we mainly consider the studies performed under ultrahigh vacuum conditions, but for some systems, we highlight results obtained in a different environment. Readers more interested in the electrochemical studies are advised to refer to the reviews by K. Itaya [5], O.M. Magnussen [6].

Monolayers of halogen atoms adsorbed on metal surfaces are also very attractive for studying structural phase transitions in two-dimensional systems [1]. These phase transitions can be observed at room temperatures, whereas noble gas films commonly used for such studies need cryogenic temperatures (5–80 K), which adds complexity to the experiment. In addition, as was argued by Bertel et al. in their series of works on Br/Pt(110), phase transitions in halogen monolayers could be governed by the electronic properties of the surface (see Ref. [7] and references therein).

Particular interest is also related to the product of halogen-metal reaction. Halides of noble metals are wide-bandgap semiconductors (2–3.5 eV) with specific electrical and optical properties (ion conductivity, high quantum efficiency, photo reactivity). The growth of thin (a few nanometers) halide films or halide nanoislands was found to start only after the metal surface is completely precovered with a dense chemisorbed monolayer. If halogen adsorption is better understood, it could help create a technology for growing nanosize halide crystals with unusual electrical and optical properties related to quantum size effects. Flat thin halide films appear to be promising interlayers that could decouple electronic states of adsorbates (e.g. molecular electronic states) from the metal conduction band. Flat thin films of noble metal halides could be an alternative to wide gap dielectrics (MgO, NaCl, KCl, etc.) usually used for this purpose.

For the sake of completeness, the surface chemistry of the alkyl halides and other halohydrocarbons should be mentioned. Indeed, the thermal and photoinduced reactions of these molecules on metal and semiconductor surfaces have been studied extensively in the last decades [8,9]. These studies were motivated, on the one hand, by the importance of alkyl halides as precursors in many chemical industry processes [9], and, on the other, by their high toxicity and environmental footprint [10–12].

The behavior of alkyl halide molecules on metal surface is determined by the unusually weak bond between carbon and halogens and the unusually strong bond between halogens and metals. According to numerous studies, carbon-halogen bond scission is thermodynamically and kinetically favored over carbon-hydrogen bond scission [9]. This property makes hydrocarbon halides the most extensively applied precursor for generating hydrocarbon fragments on metal surface [9]. The carbon-halogen bond can be broken either by thermal or photoinduced dissociation.

The another side of the dissociation of the halohydrocarbons is the generation of halogen atoms strongly bound with metal surface. It is noteworthy that this approach has been used in early studies of halogen/metal systems to create a chemisorbed monolayer [13–15].

In general, the interaction of halogens with metal surfaces, known as a rather complicated process, leads to the formation of the chemisorbed monolayer (ML) of halogen atoms at the first stage of reaction and to the subsequent growth of the metal halide film at the second one [1,2]. As a sequence, the thermodesorption spectrum of the halogen/metal system usually contains two peaks corresponding to the desorption of multilayers (halide phase) and monolayer (chemisorbed phase) (see Fig. 1).

Since halide is a different chemical compound, the chemical state of the halogen atom within the halide is strongly different from that in the chemisorbed phase [17–23]. This difference results

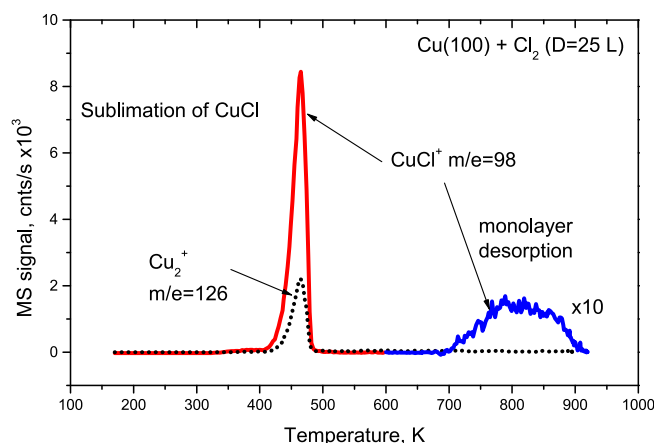


Fig. 1. Thermodesorption spectrum obtained after adsorption of molecular chlorine (25 L) on the Cu(100) surface at 160 K. From Ref. [16].

in a large chemical shift (up to several eV) in Auger electron spectra (see Fig. 2a), which, in turn, helps identify chemical states on a surface during halogenation. Indeed, it has been shown in a number of papers [17–21] that factor analysis [24,25] applied to an array

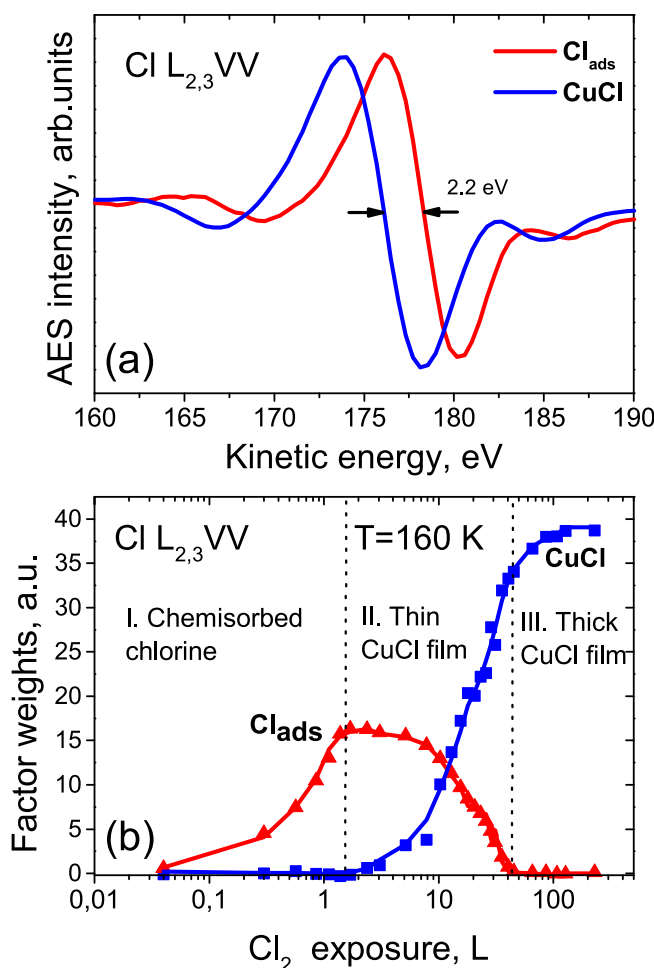


Fig. 2. (a) Profiles of Cl  $L_{2,3}VV$  Auger line acquired for copper chloride film (CuCl) and chemisorbed chlorine ( $Cl_{ads}$ ); (b) Results of AES factor analysis performed for chlorine  $L_{2,3}VV$  Auger line. The behavior of CuCl and  $Cl_{ads}$  components is indicated by squares and triangles correspondingly. Adapted from Ref. [16].

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