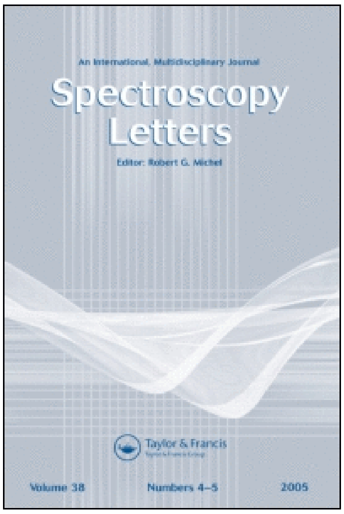
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Formation of an Oxy-Chloride Overlayer at a Bi(0001) Surface

B. Afsin[a]; M. W. Roberts[b]
[a] Chemistry Department, Faculty of Arts and Sciences, Ondokuz Mayis University, Samsun, Turkey [b] School of Chemistry and Applied Chemistry, University of Wales, Cardiff, U.K.

To cite this Article Afsin, B. and Roberts, M. W.(1994) 'Formation of an Oxy-Chloride Overlayer at a Bi(0001) Surface', Spectroscopy Letters, 27: 1, 139 — 146
To link to this Article: DOI: 10.1080/00387019408002513
URL: http://dx.doi.org/10.1080/00387019408002513

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 27(1), 139-146 (1994)

FORMATION OF AN OXY-CHLORIDE OVERLAYER AT A Bi(0001) SURFACE

Key words: X-ray photoelectron spectroscopy, oxy-chloride, H-abstraction, facile chemisorption

B. Afsin[1] and M.W. Roberts[2]

1. Chemistry Department, Faculty of Arts and Sciences, Ondokuz Mayis University,
55139 Samsun-Turkey.

2. School of Chemistry and Applied Chemistry, University of Wales, P.O. Box 912,
Cardiff CF1 3TB, U.K.

Downloaded At: 03:48 30 January 2011

ABSTRACT

A facile oxygen-induced chemisorptive replacement reaction occurs when a Bi(0001)-O overlayer is exposed to hydrogen chloride at 298K. The overlayer, which conforms to the stoichiometry $BiOCl_2$, is stable in contrast to analogous chemistry observed earlier with a Pb(110) surface. Evidence for discrete localized states associated with Bi^{2+} or Bi^{3+} species is observed from shifts in the Bi(4f) binding energies while the charge distribution within the bismuth-chlorine bond is shown to be sensitive to the presence of oxygen adatoms within the oxy-chloride overlayer.

Copyright © 1994 by Marcel Dekker, Inc.

INTRODUCTION

The activation of adsorbates and the enhancement of surface reactivity by chemisorbed oxygen at different metal surfaces has been well established[1,2] through photoelectron spectroscopy. In earlier studies[3,4] of the sp-metals silver and magnesium the activation of halogen hydrides by surface oxygen was investigated, with evidence for the electronegative chlorine adatoms participating in strong hydrogen bonding with adsorbates. Other examples of oxygen activation of hydrogen chloride leading to chemisorptive replacement of oxygen by chlorine adatoms have been reported for Cu(111) and Pb(100) surfaces.[5,6] In the latter case the chloride overlayer was found to be metastable reverting *suddenly* to the clean metal when the surface oxygen was completely replaced. In other words the chloride overlayer was stable only in the presence of surface oxygen.

Bismuth oxide and mixed oxides of bismuth are of considerable interest in selective oxidation catalysis[7,8] while bismuth oxide combined with chlorine can be used as a highly selective oxidation catalyst.[9] Furthermore bismuth oxychlorides exhibit high catalytic activity in the selective oxidation of hydrocarbons[10,11]. The identification of oxychloride overlayers and in particular their stoichiometry and the charge distribution within the overlayer is therefore of general interest in understanding catalytic activity.

Downloaded At: 03:48 30 January 2011

EXPERIMENTAL

Photoelectron spectra were obtained using a VG ESCA-3 spectrometer. A Bi(0001) single crystal which had been mechanically polished using diamond paste and chemically cleaned using acetone, was washed and then dried prior to insertion in the spectrometer. The crystal surface was cleaned by argon ion bombardment and annealed at 470K. Spectroscopically pure oxygen was obtained from BOC Ltd in glass bottles while hydrogen chloride was supplied in gas cylinders by Matheson Gas Products. The oxygen bulb was attached directly to the spectrometer's vacuum line. Hydrogen chloride was purified on a separate vacuum line by freeze-thaw cycles, sealed into glass bottles and connected to the gas handling system. The purity of these gases was checked with a quadrupole mass spectrometer. The binding energies of the photoelectron peaks were calibrated against the clean

$Bi(4f_{7/2})$ peak at 156.5 eV[12]. The surface concentrations of various species were calculated using the equation of Carley and Roberts[13].

RESULTS AND DISCUSSION

An atomically clean Bi(0001) surface exposed to 5000L of dioxygen at room temperature shows a single O(1s) peak of 529 eV binding energy (figure 1). This is accompanied by a shift in the Bi(4f) binding energy (figure 2) and the ratio of the oxygen and $Bi^{\delta+}$ concentrations calculated from the O(1s) and Bi(4f) spectra is in a 1:1 ratio suggesting the formation of a BiO overlayer with Bi in the 2+ oxidation state. The surface was then exposed to hydrogen chloride and O(1s), Cl(2p) and Bi(4f) spectra taken. The intensity of the O(1s) peak at 529 eV decreased after 20L HCl exposure while the Cl(2p) develops intensity due to surface chloride formation [figures 1A(c) and 1B(c)]. The attenuation of the 529 eV peak is accompanied by the development of intensity at 529.8 eV.

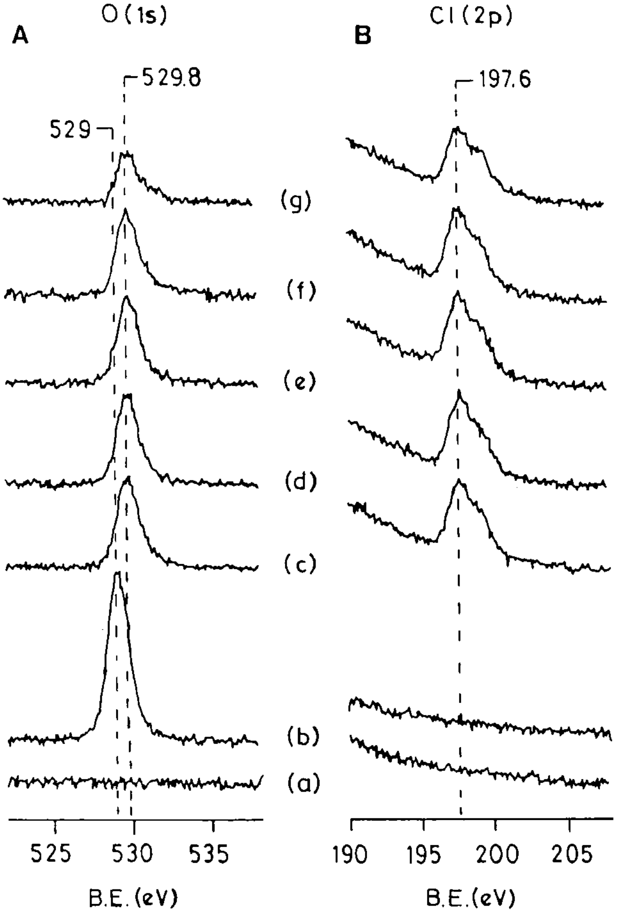
The shoulder present at 158.3 eV in the Bi(4f) spectrum [figure 2A(b)] is therefore assigned to the Bi^{2+} component. The chemical shift between Bi^0 and $Bi^{\delta+}$ components increases from 1.8 eV to 2.7 eV as the Bi^{2+} species are replaced and resulting in the shifted and relatively broader Bi(4f) spectrum with peaks at 159.2 eV and 164.5 eV revealed in the Bi(4f) differ3ence spectrum (figure 2B). These shifted peaks suggest the development of a more ionic metal-ligand bond than Bi^{2+}.

The concentration of the oxygen decreased to 0.52×10^{15} atoms-cm^{-2} after the initial (20L) exposure of $HCl_{(g)}$ and continued to decrease slowly with increasing exposure (figure 3). The O(1s) and Cl(2p) peak intensities remain unchanged for $HCl_{(g)}$ exposures in the range 60-600L. The maximum chlorine concentration of 1.1×10^{15} atoms-cm^{-2} corresponds to a monolayer (figure 3). The Bi^{2+} concentration (see difference spectra figure 2) decreases only very slightly and the stoichiometry of the oxy-chloride overlayer is close to $BiOCl_2$ which is thermally stable up to at least 420K in vacuo[14]. The $BiOCl_{2(a)}$ overlayer however reacts slowly with HCl at very high exposures, the surface chloride concentration decreasing by 20% (figure 3).

Oxygen interaction with Bi(0001) clearly leads to the formation of Bi^{2+} associated with the oxide overlayer of stoichiometry BiO. Although $HCl_{(g)}$ does not interact with an atomically clean Bi(0001) surface at 298K, this overlayer

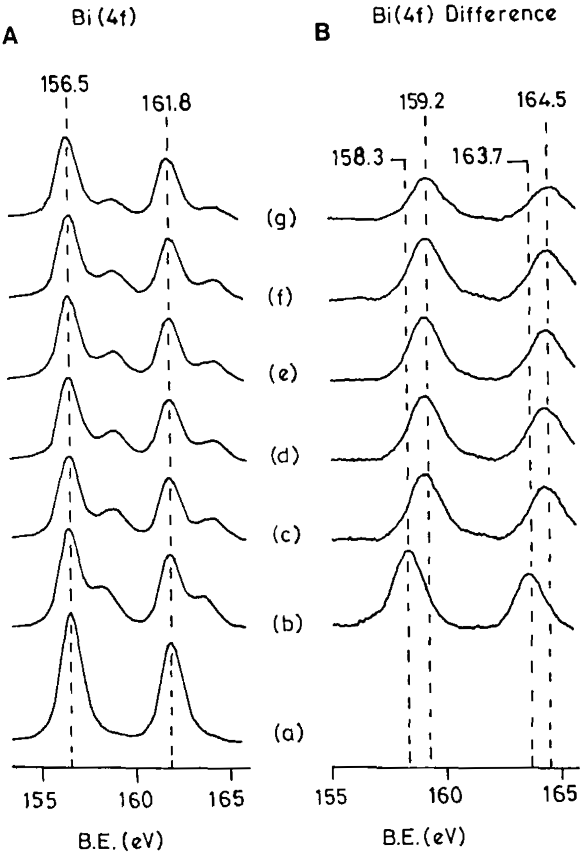
Downloaded At: 03:48 30 January 2011

Downloaded At: 03:48 30 January 2011



FIGS. 1A and 1B. XP O(1s) and Cl(2p) spectra for a Bi(0001) surface after exposure to oxygen followed by exposure to hydrogen chloride at 298K: (a) clean; (b) 5×10^3L $O_{2(g)}$; (c) 20L $HCl_{(g)}$; (d) 60L $HCl_{(g)}$; (e) 200L $HCl_{(g)}$; (f) 600L $HCl_{(g)}$; (g) 30000L $HCl_{(g)}$.

Downloaded At: 03:48 30 January 2011



FIGS. 2A and 2B. XP Bi(4f) and Bi(4f) difference spectra - with B^0 component removed - for a Bi(0001) surface after exposure to oxygen followed by exposure to hydrogen chloride at 298K: (a) clean; (b) 5x10^3L $O_{2(g)}$; (c) 20L $HCl_{(g)}$; (d) 60L $HCl_{(g)}$; (f) 600L $HCl_{(g)}$; (g) 30000L $HCl_{(g)}$.

undergoes a facile chemisorptive replacement through O-induced proton extraction and water desorption to generate a chemisorbed oxy-chloride overlayer on exposure to $HCl_{(g)}$. At room temperature the ratio of surface oxygen to chlorine atoms participating in the chemisorptive replacement reaction is 1:2 but the reaction becomes slow when the surface stoichiometry is $BiOCl_2$ (figure 3).

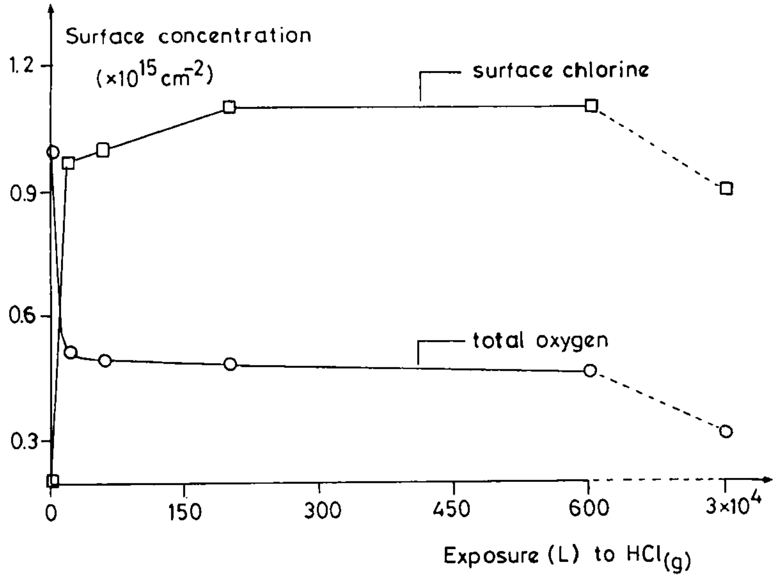


FIG. 3. The variation of surface concentrations of oxygen and chlorine species with exposure to hydrogen chloride for the interaction of HCl(g) with a pre-oxidised Bi(0001) at 298K.

Downloaded At: 03:48 30 January 2011

On further more extensive exposure to $HCl_{(g)}$ at 298K (figures 1,2 & 3) both the surface oxygen and $Bi^{\delta+}$ concentrations decrease while the chlorine concentration increases slightly. The $\sigma_{Bi}{}^{\delta+}/\sigma_{O}{}^{\delta-}$ concentration ratio remains unchanged suggesting that charge compensation is maintained within the overlayer. Clearly, each surface oxygen removed at high HCl exposures is not, under these conditions, being replaced by two chemisorbed chlorine atoms and we suggest that the chlorine within the oxy-chloride overlayer desorbs as dichlorine. In other words the reaction occurring is the oxidation of hydrogen chloride, this being accompanied by the reduction of some of the Bi^{2+} species to Bi^{0} a thermodynamically highly favourable process. The 2.7 eV shift in the Bi(4f) peaks (figure 2) with respect to those characteristic of the clean metal indicates that the oxy-chloride overlayer is highly ionic in character. Such large shifts nearly 3 eV, in metal substrate peaks are not usually observed in the chemisorption of simple diatomic molecules and suggest the presence of high oxidation state Bi^{3+} species. The ratio of surface chlorine to bismuth atoms in the highest oxidation state is 3:1 which further supports the presence of $BiCl_3$.

When the oxide species are removed at high HCl exposures (figure 3) the electron density at the chlorine adatoms is suggested to increase in order to maintain charge neutality. In other words the chlorine originally present within the 'oxy-chloride' overlayer has, with loss of oxygen, become a more ionically bonded chemisorbed chlorine. Surface oxygen is therefore seen to determine not only the reactivity of the Bi(0001) surface to the halogen-hydride but also the charge distribution within the Bi-Cl bond in the oxy-chloride species.

In summary we have observed an oxygen induced chemisorptive replacement reaction generating a stable ionic bismuth oxy-chloride overlayer. The activity of the chemisorbed BiO overlayer in efficient and facile H-abstraction is compatible with the high activity of bismuth oxide in selective oxidation of hydrocarbons.[17] The results also throw some light on the mechanism of the heterogeneous oxidation of hydrogen chloride to dichlorine.

Downloaded At: 03:48 30 January 2011

REFERENCES

1. Roberts M.W. Appl. Surf. Sci. 1991; 52: 133.
2. Afsin B. and Roberts M.W. Catal. Lett. 1992; 13: 277.
3. Au C.T., Singh-Boparai S.P., Joyner R.W. and Roberts M.W. J. Chem. Soc. Faraday Trans. I 1983; 79: 1779.
4. Au C.T. and Roberts M.W. Surf. Sci. 1985; 149: L18.
5. Moroney L.M., Rassias S. and Roberts M.W. Surf. Sci. 1981; 105: L249.
6. Blake P.G., Carley A.F. and Roberts M.W. Surf. Sci. 1982; 123: L733.
7. Burrington J.D. and Graselli R.K. J. Catal. 1979; 59: 79.
8. Haber J., 8th Int. Cong. Catal. 1 85; Verlag Chemie, 1984.
9. Ueda W., Sakyu F., Isozaki T., Morikowa Y. and Thomas J.M. Catal. Lett. 1991; 10: 83.
10. Thomas J.M., Ueda W., Williams J. and Harris K.D.M. Faraday Disc., Chem. Soc. 1989; 87: 33.
11. Williams J., Jones R.H., Thomas J.M. and Kent J. Catal. Lett. 1989; 3: 247.

12. Joyner R.W., Roberts M.W. and Singh-Boparai S.P. Surf. Sci. 1981; 104: L199.
13. Carley A.F. and Roberts M.W. Proc. Roy. Soc. London 1978; A363: 403.
14. Afsin B. PhD thesis, Univ. of Wales, Cardiff: 1992.
15. Carley A.F., Hegde M.S. and Roberts M.W. Chem. Phys. Lett. 1982; 90: 108.
16. Kamath P.V., Prabhakaran K. and Rao C.N. Surf. Sci. 1984; 146: L551.
17. Graselli R.K., Burrington J.D. and Brazdil J.F. Faraday Disc., Chem. Soc. 1981; 72: 203.

Date Received: February 1, 1993
Date Accepted: August 27, 1993

Downloaded At: 03:48 30 January 2011