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Secondary ion emission from Cu(100) surfaces with atomic adsorbates (N, O, Cl, S and Br)

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ABSTRACT

Several targets that consist of atomic species X (X = N, O, Cl, S, Br) adsorbed at hollow sites on the Cu(100) surface have been examined with low-fluence secondary ion mass spectrometry (SIMS). The positive and negative secondary ion (SI) abundance distributions, which show a range of characteristics, have been discussed with the aid of thermochemical data derived from ab initio calculations. In positive SIMS, CuX^+ is never observed, while the only heteronuclear (mixed-atom) SI that is observed for all five systems is Cu_2X^+. In negative SIMS, the dominant heteronuclear species for all systems is CuX_2^-, except for N/Cu(100), which produces no CuN_k^-, ions. Cu^- emission is observed only for O/Cu(100). By analogy with results from laser ablation studies of O/Cu targets, it is conjectured that Cu^- is a daughter product of the gas-phase dissociation of polyatomic Cu–O anion clusters.

1. Introduction

The explanation and prediction of secondary ion (SI) abundance distributions is a long-standing problem that remains one of the fundamental theoretical challenges of secondary ion mass spectrometry (SIMS). Even simple targets give rise to complex SIMS spectra due to the emission of SIs that can have a range of molecular formulae. For example, a target consisting of an atomic species X adsorbed on the surface of a metal M produces cluster ions of the form $M_jX_k^{\pm}$.

There have been many attempts to establish the information content of SI abundance distributions, especially their relationship to the surface structure and composition of the target [1]. SIMS spectra for molecular solids can be rationalised using fragmentation models analogous to those used for electron impact mass spectra [2]. For crystalline solids, the most extensive experimental data have been collected for oxidised metal surfaces and bulk metal oxides [3–6], but other classes of binary inorganic compounds including sulphides [7], halides [8,9] and borides [10] have also been surveyed.

SI abundance distributions differ sufficiently with composition for crystalline targets that they can be used for speciation purposes [1,11]. The statistical properties of cluster ion series such as $MO_k^{\pm}$ from metal (M) oxide targets can be described by a normal distribution depending on the index k [3]. It has been suggested that cluster ion yields reflect variations in the valence electron number (shell structure) of the corresponding cluster ions, and can thus provide information about the bonding state of the metal atom in the oxide [12]. In another approach, structural motifs in the target have been inferred from the structures of prominent cluster ions. For example, the Ni_2^+/Ni^+ yield ratio has been used as an indicator of the structural integrity of Ni crystal surfaces [13], while M_jCO^+/M_j^+ ratios have been used to characterise the bonding configurations of CO adsorbed on metal surfaces [14]. Correlations between target and SI structures have also been identified for SIMS data obtained from compound crystals [15].

This paper compares the characteristics of SIMS spectra measured for targets that consist of an atomic species X (X = N, O, Cl, S, Br) adsorbed on a Cu(100) single crystal surface (the SIMS data for S/Cu(100) have been presented previously [16]). To aid in the discussion of the experimental data, ab initio calculations of the thermochemical properties of a range of Cu_jX_k clusters and their ions have also been carried out.

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The intention of this study was to examine the dependence of SI abundance distributions on the chemical properties of the adsorbate, while avoiding as far as possible the potentially confounding effects of structural differences. This approach is similar to that of Allen et al. who examined spinels with a range of metal atom compositions in order to separate the effects of composition changes from those of crystal structure [4]. The use of low-fluence bombardment conditions and single crystal substrates in this study ensures that the target surfaces remain structurally well-defined during the SIMS analysis. For X = N, Cl, S and Br, the high coverage adsorbate structures involve hollow site occupation, with 4-fold coordination of the adsorbate by (relaxed) surface Cu atoms [17–20]. In contrast, O/Cu(100) is a reconstructed surface and the adsorbate has only 3-fold coordination to surface, Cu atoms at the adsorption (hollow) site [21]. For X = O, Cl and Br, adsorbate coverages of about 0.5 ML can be achieved. The N/Cu(100) structure also has a theoretical maximum coverage of 0.5 ML. However, the maximum N coverage achievable via N_2^+ bombardment (Section 2) has not been established, and may be below 0.5 ML. S forms a (2×2) structure on Cu(100) that permits a maximum adsorbate coverage of only 0.25 ML. In summary, the structural environments for different adsorbates are not identical, but the similarities of structure extend to the following details: the adsorbate is located at surface hollow sites with similar primary coordination by 4 Cu atoms for all systems except O/Cu(100) (reconstructed hollow site, with 3-fold coordination), while the adsorbate surface coverages vary between 0.25 and 0.5 ML.

Early studies of cluster ion emission behaviour such as [3,5] were hampered by a lack of thermochemical data relating to clusters (which persists to this day). However, ab initio calculations of the quantities of interest have become more feasible in recent years. In this study, ab initio thermochemical properties are found to have some predictive or explanatory power for the positive cluster ion abundance distributions. Negative cluster ion abundance distributions correlate less consistently with SI thermochemical properties, and may instead reflect the abundance distributions of daughter products derived from anion dissociation processes.

2. Experimental

2.1. SIMS measurements

The Cu(100) specimen (in the form of a 1 cm diameter disc) was oriented by Laue diffraction to within 1° and then polished (1 μm diamond paste), chemically etched (HNO_3) and rinsed (water, 2-propanol) prior to insertion in the SIMS spectrometer, whose base pressure after bakeout was 10^{-10} mbar. The subsequent cleaning of the crystal in UHV involved numerous cycles of Ar^+ bombardment and heating (~1000 K), which reduced all contaminants to satisfactory levels, as determined by SIMS (e.g. for 1 nA Ar^+: C_2^-, CN^-, $Cl^- < 50$ counts s^{-1}; O^-, $C_2H^- < 10$ counts s^{-1}). Secondary ions were detected in the normal emission direction (using a 1–400 amu VG SXP400 quadrupole mass spectrometer). The angle between the primary beam direction and secondary ion emission direction was 45°. SIMS data were acquired using a rastered, micro-focussed ion source (VG AG61) with primary ion (4 or 5 keV Ar^+) current densities of 4–7 nA cm^{-2}, depending on sample SI yields. The target sample bias was adjusted to optimise the yields of cluster ion species. Overlayers of O, Cl, S and Br were prepared by exposing clean Cu(100) to reactive gases at ~320 K, which were dosed at low pressures via a leak valve. Ion-induced secondary electron current variations [22] were used to judge the saturation exposures (O_2: 200 L; Cl_2, H_2S, Br_2: 10 L), where 1 L = 10^{-6} torr s. The N overlayer was prepared by bombardment of Cu(100) with 3 keV N_2^+ ions (10 μA cm^{-2}, 300 s), followed by annealing at ~500 K.

2.2. Ab initio calculations

Ab initio calculations of cluster properties were carried out for neutral and ionic forms of CuX, Cu_2X, Cu_3X, and CuX_2 species (where X = N, O, Cl, S, Br or Cu) by means of density functional theory (DFT) using the Gaussian-03 suite of programs (revision B.05) [23]. The hybrid B3LYP exchange-correlation functional was used for the DFT calculations [24,25]. Scalar (spin-independent) relativistic effects were taken into account by employing the second-order Douglas–Kroll–Hess (DKH2) Hamiltonian [26]. For all clusters (i.e. neutrals and ions), except the C_{3v} Cu_3X^+ species, the structure optimisations and total energy calculations were carried out using the (all-electron) 6-311+G(3df) triple-zeta basis set, which is available for elements up to Kr and is supplemented by polarization and diffuse functions. Structure optimisations for the C_{3v} Cu_3X^+ species were performed using the smaller 6-31+G(3df) basis set, with a non-relativistic Hamiltonian (in order to circumvent convergence problems). Single-point energy calculations were then carried out at the optimised structure by the method employed for the other clusters.

For both Cu_2X and CuX_2 clusters, calculations were carried out for linear (D_{2h}) and bent (C_{2v}) geometries, and for CuX_2 clusters only, the bent Cu(X_2) (C_s) geometry. For Cu_3X clusters, calculations were carried out for D_{3h} and C_{3v} geometries. For Cu_j clusters, an analogous range of structures was considered, as well as the optimum structures identified by prior theoretical studies. For all atoms and clusters, the DFT calculations were carried out for the electronic states having the lowest spin multiplicities; states of higher multiplicity were also examined for a few well-established exceptions (^4N, ^3O, ^3S, $^3O_2$, $^3S_2$) and for CuX, Cu_2X, Cu_3X, CuX_2 neutrals and ions with X = N, O and S. The DFT calculations form the basis of a database of total energies for neutral and ionized clusters, that includes about 250 distinct structures or electronic states, and is used to predict the molecular properties described below for the most stable neutral and ionic cluster species.

For each optimised neutral cluster structure the properties calculated were: binding (or atomization) energies (BE), vertical ionization potentials (IP), and vertical electron affinities (EA). Where required for computations of ion dissociation energies (see below) adiabatic IPs and/or EAs were also calculated after optimisation of cluster ion structures. The calculations neglect zero point energy corrections, which contribute less than 0.05 eV to relative energies. Results are reported only for the most stable geometry of each molecular formula. During a vertical transition the structure of the cluster does not change, but for clusters containing N, O or S atoms, the spin multiplicity may increase or decrease (the final state multiplicity that yields the smallest IP or largest EA is chosen).

Dissociation energies (D_+, D_-) for Cu_jX^+ and CuX_k^- cluster ions are estimated from the DFT results by consideration of the energetics of all possible dissociation processes that involve loss of a monatomic species (atom or ion) from the parent ion (the most facile process being chosen). For example, 6 such dissociation processes are possible for Cu_3X^+. The estimates of D_+ and D_- are based on the energies of the optimised ground state structures of each species (neutrals, ions) that appears in the dissociation scheme. The most facile $Cu_jX_k^{\pm}$ dissociation processes are found to be as follows: $CuX^+ \rightarrow Cu^+ + X$; $Cu_2X^+ \rightarrow Cu^+ + CuX$; $Cu_3X^+ \rightarrow Cu + Cu_2X^+$ (except $Cu_3N^+ \rightarrow Cu_3^+ + N$); $CuX^- \rightarrow Cu + X^-$ (except $CuN^- \rightarrow Cu^- + X$); $CuX_2^- \rightarrow CuX + X^-$ (except $CuO_2^- \rightarrow Cu^- + O_2$).