Inelastic ion-surface collisions: Understanding secondary emission of molecular ions

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Abstract. Electron transfer phenomena and inelastic ion-surface collisions lead to various processes of ionization: excitation of projectile/target atoms, secondary electron or atom/ion emission, etc. An important issue is the effect of electron exchange between the outgoing excited/ionized species and in particular, the effect of the chemical environment or surface composition on the outcome of the emission process. Secondary emission of molecular and/or cluster ions in the sputtering process has a large impact on the compositional analysis of materials. The problem arising out of ‘matrix effect’ in secondary ion mass spectrometry (SIMS) has largely been circumvented by the quantitative potential of the MCs⁻⁺SIMS method. However, it generally suffers from a low useful yield of MCs⁺ ions and in such case, MCs⁺₂ molecular ions offers a better detection sensitivity. The present paper addresses the understanding of MCs⁺ⁿ (n = 1,2,...) molecular ions formed in inelastic ion-surface collision processes.

1. Introduction

The analysis of surfaces, interfaces and bulk materials through ion beam induced sputtering is a mature and well-established technique. The ejection of surface atoms or molecules under energetic ion impact (in the range of few hundred eV to several MeV) is estimated primarily by the ‘sputtering-yield’ (defined as the mean number of emitted atoms per incident ion) and in this process, the bombarding ion transfers energy in collisions to target atoms, which recoil with sufficient energy to generate other collisions. Some of the backward recoils in the generated ‘collision cascade’ impart enough energy to the surface atoms enabling them to overcome the surface binding energy and to escape from the solid. Therefore, the secondary sputtered species originate from the collision cascades that are created within the target lattice and from recoil sputtering.

In the linear cascade regime, the sputtering yield is proportional to the number of recoil-atoms that is proportional to the energy deposited per unit depth in nuclear processes (particle velocity much less than the Bohr velocity). Effective thickness of the sputtered layer arising out of a single collision cascade is of the order of an atomic dimension and its estimate can be obtained from a simple expression of the sputtering-yield involving information depth, typical average energy of the sputtered particles and nuclear stopping power [1]. As the ejected particles stem essentially from the outermost (∼ 1-3) atomic layers, they carry information about the composition of the near-surface region. The varieties of the sputter-products constitute electrons, atoms, atomic...
clusters, molecules ‘in tact’ and distinctive molecular fragments. A very small fraction of the sputtered atoms or molecules may be ionized, either positively or negatively, and/or excited above their respective ground states. The atoms (or ions) sputtered in the excited states may subsequently go through two inelastic processes:

I. Radiative electronic transition via de-excitation of the excited neutral (or ionic) species leading to the emission of photons in the range ultra-violet to visible optics.

II. Non-radiative electronic transition leading to the emission of Auger electrons or to the ionization of the sputtered species via resonant-tunneling of electrons from these species to the valence band of the solid.

The above dynamic charge-transfer processes occurring between the escaping sputtered atom and the solid surface are further complicated by the strong electronic and structural perturbations from the ion bombardment.

2. Secondary ion emission and Matrix effect

Secondary emission of ions as well as photons in the sputtering process is an inelastic phenomenon in ion-surface interactions and has tremendous important applications in materials analysis. Analytically, one of the important sputtering techniques based on the above phenomenon is the “Secondary Ion Mass Spectrometry” (SIMS), in which the ionized fraction of the sputtered species (known as secondary ions) is detected by a mass spectrometer equipped with appropriate ion collection optics. Figure 1 shows the schematic representations of the technique. In this technique, the primary beam removes atomic (molecular) layers of the sample at a rate determined by the intensity, mass and energy of the bombarding ions and by the physical and chemical characteristics of the sample itself.

![Figure 1. Schematic diagram of the SIMS technique.](image)

Despite the highest detection sensitivity (∼ part-per-billion level) and excellent depth-resolution (down to less than ∼ 2 nm) of SIMS, the technique suffers from the “matrix effect” (variation of the ionization probability of a certain species due to the instantaneous change in local surface chemistry of the target containing the species) which hinders the quantification. A typical matrix effect was demonstrated through SIMS investigations of Pt/Cu and Au/Cu multilayers [2], where the large humps for Pt and Au signals across the interface positions in the respective multilayers are due to the preferential trapping of oxygen in these multilayer structures. Obviously, the matrix effect requires to be appropriately compensated while estimating the actual concentration of a certain species present in the host (‘matrix’). The compensation is usually done by using “calibration standards”, “relative sensitivity factor” (RSF) approach etc. The use of ‘ion-implanted standards’ has reached a
high level of sophistication, allowing precision measurements in SIMS quantification. From an analytical point of view, motivation towards the reduction of the matrix effect has led to the development of another technique called “secondary neutral mass spectrometry” (SNMS). But basically the very fact that sputtered neutral signals are far less intense than the secondary ion signals has led most of the workers to concentrate on the secondary ion emission process for analytical work, despite the complexities in the ionization mechanism. Although quite sophisticated theoretical treatments of the ionization process have been developed for idealized models [3, 4], a quantitative theory that takes into account the dynamic evolution of the sputtering collision cascade and the chemical complexity of real materials is not yet available.

3. Molecular ion emission: possible mechanisms

3.1. MCs$^+$ ions

The most useful and promising technique to reduce the matrix effect in SIMS analysis seems to be the MCs$^+$ technique. Under Cs$^+$-bombardment, it has been shown that detection of the element $M$ of interest by monitoring of MCs$^+$ molecular ions (instead of conventional $M^-$ ions) is largely unaffected by changing matrix [5], thereby enabling this mode of analysis possible to quantify without the aid of calibration standards [6, 7]. Although the application of this technique is difficult for its poor sensitivity (MCs$^+$ molecular species are usually less abundant than the atomic ions), MCs$^+$ detection scheme is more favorable in cases where matrix effects are most severe, particularly for major components. This novel technique is referred to as Cs$^+$-assisted secondary ion mass spectrometry or simply as MCs$^+$-SIMS [8] and has been successfully utilized in a study of Pd-Rh interdiffusion which has a relevance in brachytherapy. Different Rh$_x$Pd$_{1-x}$ layers were deposited by PVD and were subsequently characterized by ToF-SIMS. A linear relationship between the relative CsPd$^+$ yields and Pd concentration into the Rh matrices enabled to calibrate the ToF-SIMS depth profiles of annealed Pd/Rh layers and hence to quantify the PdRh interdiffusion [9].

Formation mechanisms of MCs$^+$ secondary ions and the analytical applicability of MCs$^+$-SIMS technique have been examined by several workers [10, 11]. Based on some experimental observations, it was proposed that MCs$^+$ ions form via a combination of independently sputtered neutral $M$ atoms and Cs$^+$ ions. Therefore, it is obvious that the binding energy between $M$ and Cs (either charged or neutral) plays a very important role in the formation of MCs molecule and in that case, the polarizability of $M$ plays the key role in the binding strength of the two species, since the interaction is basically between the electric field of Cs$^+$ and the ion-induced dipole moment of $M$. The interaction between Cs$^+$ and a polarizable neutral atom (or molecule) has been successfully modeled by applying a potential of the form

$$V(r) = A r^{-12} - 0.5 \alpha e^2 r^{-4}.$$  

(1)

where $r$ is the distance between the neutral atom and the Cs$^+$ ion, $\alpha$ is the polarizability of the former and $A$ is a constant which characterizes the repulsive term. For a variety of semiconductors, MCs$^+$ yield was found to have a quadratic dependence on the polarizability of the atom $M$ [12].

Secondary emission of atomic and molecular ions from elemental molybdenum surface has been studied under Cs$^+$ bombardment to explore the MCs$^+$ formation mechanism with changing Cs surface coverage [13]. Integrated count of MoCs$^+$ shows a monotonic increase with increasing primary ion energy. Change in MoCs$^+$ intensity is attributed to the variation of surface work function and cesium surface concentration $c_{Cs}$ due to varying impact energies (inset of Fig. 2). Variation of $c_{Cs}$ has been obtained from the expression, $c_{Cs} \propto 1/(1 + Y)$ where $Y$ is the
elemental sputtering yield. Systematic study of the energy distributions of all species emerging from Mo target has been done to measure the changes in surface work function. Changing slopes of the leading parts of Cs+ energy distributions suggest a substantial depletion in surface work function with decreasing primary ion energies. As evidenced in (Fig. 2), surface work function showed a linear dependence on \( c_{Cs} \). The maximum reduction in surface work function (\( \sim 0.69 \text{ eV} \)) corresponds to the highest value of \( c_{Cs} = 0.5 \). Emission of all atomic and molecular ionic species has been found to be consistent with the electron tunneling model. Furthermore MoCs+ formation were found to consistent the recombination model.

3.2. MCs+ ions

MCs+ method suffers from a generally low useful yield, particularly for the electronegative elements. In such cases, detection of MCs+ molecular ions offers a better sensitivity to that of MCs+ ion, as the yield of MCs+ ions has been observed much higher than that of MCs+ ions [14]. Monitoring of MCs+ could be important for the species where MCs+ emission intensity is very small. The higher emission of MCs+ is surprising as the yield of Cs+ ions is significantly less than that of Cs+ ions under identical Cs bombardment conditions. Holliger et al. [15] investigated the analytical usefulness of monitoring MCs+ ions for semiconductor profiling of n-type dopants such as P, Ge or As with a primary (Cs+ beam) impact energy of 1 keV. They indicated that the MCs+ technique has an advantage over the MCs+ technique of providing higher useful yields for electronegative elements by up to \( 10^2 \) and can therefore be applied to perform more precise junction measurements in terms of concentration, dose, decay length and detection limit.

Higher yield of MCs+ compared to MCs+ has been supported by an observation in case of Cu with varying impact ion energies [16] where the intensity ratio \( I(\text{MCs}^+) / I(\text{MCs}^+) \) was found to be greater for lower impact energies. This is understandable from the fact that Cs surface-ion concentration becomes appreciable at low impact energies thereby leading to an enhanced formation of MCs+ ions compared to that of MCs+ ions. The fact that Cs concentration on the surface changes with impact Cs+ ion energy was clearly evidenced from the kinetic energy distributions of MCs+ ions [16].

Formation mechanism of MCs+ is still not clear. Probable recombination mechanisms may be the following:

\[
\begin{align*}
\text{MCs}^0 + \text{Cs}^+ & \rightarrow \text{MCs}^+ \\
\text{M}^- + \text{Cs}^+ + \text{Cs}^+ & \rightarrow \text{MCs}^+ \\
\text{M}^0 + \text{Cs}_2^+ & \rightarrow \text{MCs}_2^+ \\
\text{M}^0 + \text{Cs}^+ + \text{Cs}^+ & \rightarrow \text{MCs}_2^{++} \rightarrow \text{MCs}_2^+
\end{align*}
\]

The first route indicates the recombination of a neutral MCs0 molecule with one Cs+ ion. The second mechanism suggests the vacuum recombination of sputtered M− ion with two Cs+ ions. These two mechanisms have been shown to be dominant for electronegative elements. The third mechanism indicates the recombination of sputtered M0 atom (neutral) with a sputtered Cs2 dimer [17]. The fourth route suggests the formation of MCs2++ ion by the association of one M atom with two Cs+ ions, followed by the conversion to MCs2+ ion via an electron capture. In this case higher Cs concentration at the surface should favor the production of MCs2++ ions. In order to check the validity of this route, detection of MCs2++ was attempted with Cu for 1 keV Cs+ impact energy and the emission of CuCs2++ was evidenced although in a very small quantity [16]. The weak intensity of CuCs2++ ions could be due to the immediate conversion from CuCs2++ to CuCs2+. Investigation on the formation of MCs2+ molecular ions under Cs+ bombardment of silver surface in the SIMS process was reported under varying oxygen environments [18]. Energy distributions of MCs+ and MCs2+ ions have shown a remarkable dependence on the changing oxygen environment. The changes in the intensities of the above molecular species are attributed
to the changes in the respattered Cs$^+$ intensity due to the decrease in the local surface work function. The MCs$^+$ molecular ion has been found to form via the recombination of a neutral M$^0$ atom with a Cs$^+$ ion and its formation probability remains unaffected by changing oxygen environment. A systematic study on the kinetic energy distributions of secondary Cs$^+$, Cs$_2^+$, MCs$^+$ and M$^0$Cs$_2^+$ ions and the estimation of the mean emission energies of various constituents participating in the respective formation processes confirm that the M$^0$Cs$_2^+$ molecular ion formation via recombination of a neutral M$^0$ molecule with a Cs$^+$ ion is the most probable one [18].

![Figure 2. Change in work function for varying cesium surface concentration. Inset: $\Delta \phi$ as a function impact energy [13].](image)

![Figure 3. Change in surface work function $\Delta \phi$ as a function of O$_2$ pressure [22].](image)

However, explanations towards the formation mechanism of MCs$_2^+$ ions according to the second route were given from the kinetic energy distributions of MCs$^+_n$ ($n = 0, 1, 2, 3, .., \text{etc.}$) molecular ions for various metallic samples (Al, Cu, and Ag) under varying Cs$^+$ impact ion energies (1-5 keV) [19]. From the peak shifts of the energy distributions it was argued that the surface binding energy as well as the work function changes with the change in the surface Cs concentration arising out of the variation in the impact ion energy. The dependence of the measured integrated yields of the ions (M$^+$, MCs$^+$, and MCs$^+_2$ for individual elements) on the estimated work functions were found to be exponential. Results were interpreted in terms of the relative changes in the instantaneous local work function of the sputtered zone. The study was strongly supportive of the suggested formation mechanism of a M$^0$Cs$_2^+$ molecular ion via a combination of M$^-$ and two Cs$^+$ ions in the close proximity of the Cs-covered surface [19].

Recently, the ionization processes of elemental and cluster ions have been studied by co-sputtering cesium and xenon on silicon wafer with cesium beam concentration varying from the 0% (for pure xenon) to 100% (for pure cesium). The observations on MCs$^+_n$ signals were explained by using electron tunneling model [20]. Although the formation mechanisms of the MCs$^+_2$ clusters are unclear, the analysis of MCs$^+_n$ clusters on organic matter provides two potential applications. First, molecular information is preserved in the MCs$^+_2$ mode allowing organic depth profiling. Second, the charge state selection (neutral, singly or doubly negatively charged) occurring during the cluster formation may offer some new information carried by neutrals or multiple charged ions [21].

A recent study on the emission of MCs$^+_n$ ($n = 1, 2, \text{...etc.}$) molecular ions from silver has been done under the joint influence of electropositive (cesium) and electronegative (oxygen)
elements [22]. The kinetic energy distributions, measured for Cs+, Cs2+ , AgCs+ and AgCs2+ ions at different oxygen pressures exhibited changing slopes in their leading parts that hinted appreciable changes in the surface work function (Fig. 3). The maximum observed change in the surface work function was 0.44 eV. The integrated counts of Cs+, Cs2+ , AgCs+ and AgCs2+ ions exhibit an exponential dependence on the surface work function, supporting the electron tunneling model of secondary ion emission. Cs2+ ion intensity has been found to be consistent with recombination of neutral Cs0 with Cs+ ion. Study of AgCs+n+ molecular ions also reveals the fact that the intensities of such molecular species are strongly affected by the oxygen environment. Variation in the Cs+ intensity due to the change in oxygen environment has been found to be a key-factor behind AgCs+n+ intensity variation. The linear dependence of AgCs+ intensity on the ionization probability of Cs+ ions strengthens the belief that an AgCs+ is formed via combination of a neutral Ag atom with a Cs+ ion in the near-surface region. Furthermore, a linear dependence of AgCs2+ intensity on the ionization probability of Cs+ suggests that AgCs2+ molecular ion formation via the combination of neutral AgCs0 molecule and Cs+ ion is the most probable one in the present situation.

4. Summary

The problem arising out of ‘matrix effect’ in secondary ion mass spectrometry (SIMS) has largely been circumvented by the quantitative potential of the MCs+−SIMS method. However, it generally suffers from a low useful yield of MCs+ ions and in such cases detection of MCs2+ molecular ions offers a better sensitivity. Formation of MCs+ is rather straightforward. The well accepted mechanism is basically via an interaction between Cs+ ion and the ion-induced dipole moment of a M0 atom. Whereas, the formation mechanism of MCs2+ molecular ion is not yet clear. The two probable routes, one as a combination of two Cs+ ions with one M− ion and the other as a combination of MCs0 molecule with a Cs+ ion, both valid for electronegative elements, have been discussed as per literature survey.

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