INITIAL ENERGY DISTRIBUTIONS OF SECONDARY IONS IN ELECTRONICS SPUTTERING

UDAYA KANTHI ABEYWARNA

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Abstract

This thesis presents measurements on kinetic energy of secondary ions desorbed from surfaces by MeV ion bombardment. The aim of this investigation is to get a deeper understanding of the mechanism of fast heavy ion induced electronic sputtering from solid surfaces. An interesting feature of this mechanism is its ability to eject intact, heavy, fragile and thermally labile biomolecules into the gas phase. This effect has an exciting application in biological mass spectrometry, as many compounds of biologically interest are difficult to ionize and desorb into the gas phase without being fragmented. In fact, in the early eightieth electronic sputtering was the only mass spectrometric ionization method to study peptides and small proteins.

Since the discovery of fast heavy ion induced desorption, attempts have been made to understand the mechanism behind the process. In the desorption event, the ion formation mechanism may be different for different kinds of ions. The molecules may be ionized directly in the ejection process or at a later stage in the gas phase. The experimental observations related to the ionization process are limited in the literature. An attempt to study this issue is carried out in the present study.

One of the physical parameters which is associated with the desorption process is the kinetic energy gained by the secondary ions ejected from the surface. In this study, a plasma desorption time-of-flight (TOF) mass spectrometer (PDMS) has been employed to measure this energy distribution of secondary ions, and the term 'initial axial energy distribution' is used throughout this thesis instead of 'energy distribution' to differentiate it from (kinetic) energies gained by secondary ions in the flight path of the mass spectrometer. Two independent experimental methods to measure the initial axial energy distributions have been developed using two types of TOF mass spectrometers, namely a linear type and a reflectron type. In the linear method, the initial energy distributions are obtained directly by converting the measured time distributions for the ions of interest. In the reflectron method, the cut-off property of an ion mirror is used to make relative measurements of the initial energy distribution. An analytical procedure has been devised in order to extract the initial axial energy distributions with a high accuracy for both positive and negative secondary ions. Mean value of the initial axial energy of positive secondary ions of H^+, H_2^+, $^6Li^+$, $^7Li^+$, Na^+, and Cs^+ thus measured are found to be 4.9 eV, 4.8 eV, 1.1 eV, 1.3 eV, 1.5 eV and 3.3 eV respectively while the negative secondary ions of H^-, OH^-, and F^- are found to be 0.6 eV, 0.9 eV and 1.1 eV respectively. The experimental errors due to field leakage, a second order effect, have been carefully examined and the necessary corrections have been made.

Several of measured energy distributions exhibit tails extending towards energies lower than the corresponding acceleration potential in the TOF mass spectrometer indicating an energy deficit. The degree of tailing depends upon the nature of the desorbed ions. A fraction of the desorbed ions has thus less kinetic energy than value expected from the acceleration voltage. This suggests the possibility of a gas phase ion formation mechanism in fast heavy ion induced desorption. By deconvoluting the converted energy distributions, which are obtained from the experimental time distributions, it has been found that the measured initial

axial energy distributions consist of two components; one component associated with the desorption of secondary ions from the target surface, and the other with the ions formed in the gas phase after the desorption event. The possibility of a separation of ionisation events into these two categories is also theoretically examined in the thesis. Using experimental observations, the time and place of ion formation of the secondary ions are also suggested.

Analysis of the experimental results suggests that the initial axial energy distributions of the secondary ions studied in the present work closely follow a semi empirical function of the form $E^2\exp(-E/E_0)$, where E_0 is a constant. This indicates that the desorption mechanism of the studied secondary ions exhibits a common ejection mechanism. This finding is in agreement with the experimental results of the studies performed by varying the energy density of the primary ion track (i.e. variation of the stopping power) while keeping the track dimensions constant. The latter results showed a linear dependence of the full width at half maximum (FWHM) of the initial axial energy distribution as a function of the stopping power supporting some predictions described in a thermal desorption.