Perspectives of Quantitative Depth Profiling

Biswajit Saha[1*] and Rajiv K. Chouhan[2]

[1]*Department of Basic Science and Humanities, University of Engineering and Management (UEM) B/5, Plot No. III, Action Area - III, Newtown, Kolkata 700156 and*

[2]*School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, USA*

This article primarily deals with the compensation of "matrix effect" in secondary ion mass spectrometry (SIMS) for direct quantitative analysis of materials using MCs^+-SIMS approach. Emphasis has been given on exploring the formation mechanisms of MCs_n^+ (n = 1, 2,..) molecular ions (M denotes the element to be analyzed and Cs^+ is the bombarding ion) emitted in the SIMS process. Following a brief introduction on SIMS, a study on MCs_n^+ molecular ions emitted from various metal and semiconductor targets under Cs^+ primary bombardment has been discussed.

I. INTRODUCTION

The rapidly growing importance of advanced materials stems from the ever-increasing importance of thin films. For example, some fast developing areas are: thin film structures for microelectronics with tailored electrical properties, optical films with specific anti-reflecting and transparent properties, coatings and beam modified surfaces with high resistance to wear and corrosion etc. Controlled fabrication of these films requires a detailed and reliable, spatially-resolved chemical and structural analysis. In view of their planar structure, the analysis of in-depth distributions of chemical composition with high resolution is of primary importance, particularly near surfaces and interfaces. For this purpose, numerous methods have been developed during past five decades [1, 2]. Among these, micro-sectioning techniques based on sputtering in combination with surface analysis methods are most frequently applied [1- 8] because they are applicable to practically any kind of materials and allow the attainment of optimum depth resolution (down to a few atomic monolayers) over a wide depth range up to several micrometers. There are many techniques available for performing an analysis of the elemental, chemical and physical makeup of a material. Many of these techniques are inexpensive to set up and operate, others are easy to interpret and some provide an absolute measurement capability. In short there is a large spectrum of techniques open to someone who wishes to do materials analysis of a sample. Each of these techniques has its own pros and cons and each its own niche. Conventional Ion Beam Analysis (IBA) techniques are far from the cheapest techniques to apply and can be complex to interpret. The scientific world has become more sensitive to costs and employing an expensive technique when a cheaper one would do is not a sustainable option.

Consequently, for IBA techniques to continue to be used at the forefront of research they must be seen to be providing something more than can be achieved via other methods. This might be in terms of the quality of the data, the speed of analysis (thereby effectively reducing the cost) or simply the only way to obtain a particular measurement.

Properties of material interfaces on atomic scale govern a great number of material properties and macroscopic phenomena. For example, structure and composition of surfaces (i.e. solid/vacuum interfaces) are responsible for all kinds of interaction of solids with ambient media as observed in adsorption, oxidation, corrosion, catalysis, friction and wear. Material properties such as brittle fracture, creep and re-crystallization are governed by the structure and composition of internal interfaces, for example, grain boundaries. In layered thin-film structures, the mechanical, thermal and chemical stability of interfaces between different materials (hetero-interfaces) is the way to reliable performance of many technological products such as microelectronic devices, sensors, components and protective coatings in various instruments, tools and medical prosthetics technologies. Despite the recent progress in interface science and technology, many details of the correlation between macroscopic physicochemical behaviour and microscopic property/composition/structure relationships of interfaces is not yet sufficiently well understood. The key to the study, control and optimization of interfacial properties appears to be a close link between the preparation and synthesis of interfaces and their chemical and structural characterization.

In particular, interfacial microchemistry is significant for the properties of interfaces [9]. The primary aim of the chemical analysis of interfaces is to determine their elemental composition and that of their surroundings with high spatial resolution, ultimately over atomic dimensions. Among the various techniques developed for this purpose, surface and interface analysis methods in combination with ion sputtering [5, 10-13] are most frequently applied because they are applicable to almost any kind of solid materials and allow the attainment of optimum depth resolution in the atomic monolayer region over a wide depth range up to several micrometres. In the context of sputter depth profiling, secondary-ion mass spectrometry (SIMS), secondary-neutrals mass spectrome-

*e-mail : biswajit.saha@uem.edu.in

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try (SNMS), glow discharge spectroscopy (GDS), Auger electron spectrometry (AES), x-ray photoelectron spectroscopy (XPS), ion scattering spectrometry (ISS) have always found their place among the most important methods for surface and interface analysis [1, 14].

Today, depth profiling using surface analysis methods in combination with ion sputtering has attained a high degree of maturity. Refinements of instruments and experimental techniques have led to great improvements in depth resolution. Instrumentation for depth profiling requires a source of energetic ions impinging on the sample surface and a suitable means of analysis of either the sputtered material or the residual surface after a certain sputtering time, as schematically depicted in Fig. 1. The ion source is usually an ion gun with beam raster facility, or low-pressure DC or RF plasma from which the ions are extracted. Analysing the sputtered particles (ions in Secondary Ion Mass Spectrometry (SIMS) or neutrals in Secondary Neutral Mass Spectrometry (SNMS)) in a mass analyzer during primary-ion bombardment yields direct information about the sample composition with depth. Alternatively, the optical emission of excited species can be determined by an optical spectrometer: Glow Discharge Optical Emission Spectroscopy (GDOES).

The complementary method is the analysis of the residual surface, for example, by electron or x-ray excitation and measurement of the secondary Auger- or photoelectron spectra with a charged-particle energy analyzer (AES and XPS). The latter can also be used for elemental analysis of the first surface layer by the determination of the primary ion energy loss due to surface scattering, as performed in Ion Scattering Spectroscopy (ISS). The basic procedure of depth profiling consists of recording the element specific peaks detected with the respective analyzer as a function of the sputtering time. For constant ion energy and beam current density the latter is proportional to the sputtered depth if the sputtering rate does not change with time.

Bombardment of a surface with energetic primary particles leads to surface erosion by emission of secondary particles from the sample. By continuous sputtering, layers beneath the original surface are subsequently exposed. Hence there are two ways to obtain the in-depth distribution of composition as a function of the sputtered depth: either by mass spectrometric analysis of the sputtered matter, as in SIMS and SNMS, or by chemical analysis of the remaining surface, as in AES, XPS and ISS in conjunction with sputter erosion of the material [2, 8]. These methods are markedly different with respect to elemental specificity and sensitivity, dynamic range, information depth etc. The sputtering process itself, however, is independent of the analysis method and should therefore be considered as a separate physical process.

Sputtering can be accomplished by removing atoms from the top monolayers of a solid [15, 16]. Therefore, a depth resolution in the monolayer regime should in principle be achievable. However, sputtering does not occur by an ideal layer by layer removal but is the result of a complex ion beam - sample interaction process. This process introduces a variety of distortional effects into the original morphology and composition of a sample, which are the cause of the much more extended profile broadening generally observed.

Recent progress in understanding the main physical processes and parameters involved in sputter erosion as well as its implications in specific surface analysis methods has led to a general framework of optimized profiling conditions for the achievement of high depth resolution. Glancing incidence of the ion beam (e.g. 80 to the normal to the sample surface) and low ion energy (< 1 keV) have pushed the depth resolution to its physical limits [6, 13, 17]. For this purpose low-energy (200 eV) ion guns with high current density have recently been developed [18]. Alternatively, molecular ions at higher energy can be applied because on impact the total energy is divided between the different atoms of the dissociating molecule [19], thus achieving a total depth resolution of 1.4 nm. In general, depth resolutions below 2 nm can now routinely be attained. In addition, the deconvolution of depth profiles by an experimentally determined resolution function is increasingly coming into use and enables us to reconstruct the original profiles with a precision of about one atomic monolayer [20-27]. Depth profiling is performed by ion bombardment of a selected area of a sample and subsequent analysis of a smaller area centred within the rastered area to avoid crater edge effects. A prerequisite for a meaningful in-depth analysis is a laterally homogeneous elemental distribution in planes parallel to the surface within the analyzed area. The experimental result consists of an elemental signal intensity as a function of the sputtering time (or the primary ion dose, in case of a calibrated ion beam current density).

In general, these raw data represent a more or less distorted image of the original, true in-depth distribution of composition. To obtain the latter, three fundamental tasks have to be solved [4-7]: (a) conversion of the sputtering time into depth, (b) conversion of the signal intensity from the surface compositional analysis method into concentration, and (c) assessment and correction of the shape distortions of a sputter profile, particularly near steep concentration gradients. These distortions limit the precision of a measured profile as described by the resolved depth, which is commonly identified as depth resolution z. These three problems are closely interlinked and can only be considered separately in a first order approximation.

II. SECONDARY ION MASS SPECTROMETRY

The fundamentals in Secondary ion mass spectrometry (SIMS) were laid by Herzog and Viehboeck (1949) [28]. Honig (1958) [29] constructed the first complete secondary ion mass spectrometer capable of sputter depth profiling. The first commercial SIMS for micro-analytical applications was introduced by Liebl (1967) [30]. Ap-

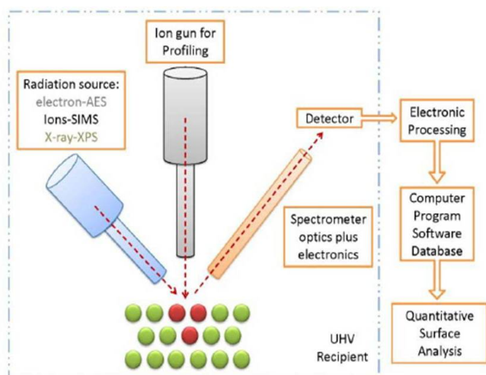

FIG. 1: Schematic showing instrumental parts and principal arrangement of a surface analysis instrument for sputter depth-profile analysis.

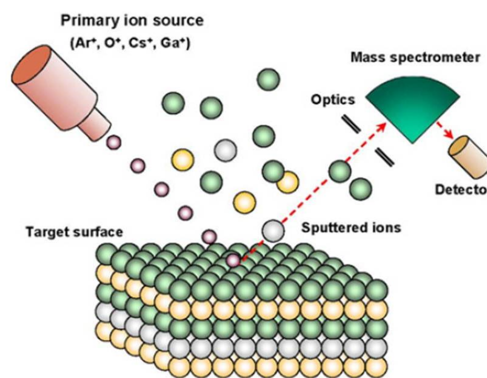

FIG. 2: Schematic layout of secondary ion mass spectrometry.

plications to semiconductor and thin-film analysis were shown by Werner (1968) [31] and depth profiling of thin surface layers was successfully demonstrated by Benninghoven (1969) [32] by the development of the static SIMS method.

Figure 2 shows the schematic representations of the technique. In this technique, the primary beam removes atomic 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. SIMS has evolved towards a cornerstone in many materials studies within the semiconductor community due to its excellent sensitivity, quantification accuracy and depth resolution. In recent years its application has expanded from simple, relatively deep dopant profiling in a single matrix towards the analysis of very shallow (¡10 nm) profiles contained in complex structures and buried below (ultrathin) metallic films (which are used as gate or silicide material). These changes have increased the demand for SIMS with very high depth resolution considerably [33]. Moreover SIMS starts to be used to study the material interactions within these structures. Whereas the original quantitative success of SIMS was based on its use within the dilute limit i.e. the analysis of a minor (low level) constituent in a single matrix, the present applications have evolved towards the analysis of very high concentration levels and matrix compositions, thereby violating the basic assumptions put forward originally to quantify SIMS results accurately. Evidently, changes in ionization probabilities and sputter yields occur when going from one matrix to another one, thereby requiring complex data treatments and calibration procedures [34, 35]. Based on these observations it is clear that one needs to consider all the fundamental SIMS mechanisms contributing to the quantification, depth scale errors and depth resolution. The mechanisms underlying the potential errors can be identified by realizing that in addition to the desired process (i.e. the mass analysis of a sputtered, partially ionized, particle flux which can be converted into an intensity profile) concurrent processes occur. Indeed the energy deposition by the primary ion leads to the development of a collision cascade which induces not only the sputter process but also causes at the same time many atomic displacements and thus a modification of the (instantaneous) internal profile.

Although the collision cascade is determined by the primary ion-matrix combination, the obtainable depth resolution for different elements is element specific [36]. This can be rationalized by considering the important mechanisms involved:

(1) The extent of the collision which determines the depth over which layers are intermixed. Obviously a larger mixing depth will mean a larger decay length. This mixing depth will scale with the primary ion energy (and penetration depth) leading to the universally observed scaling of the decay length with energy. (2) The amount of energy deposited within the collision cascade. Indeed when comparing similar penetration depths for different primary ions, these can only be achieved with higher/lower energy for the heavier/lighter ion. Hence, the energy deposition density and thus the number of displacements induced will be different. As long as the mixing has not yet led to a completely homogenized mixed layer, more displacements will imply longer decay lengths. (3) The energy transfer between a recoiling matrix element and the impurity and the distance traveled by this element for a given energy transfer. Both effects are element specific and cause the observed differences in decay lengths.

III. MATRIX EFFECT IN SECONDARY ION MASS SPECTROMETRY

Secondary emission of ions in the sputtering process is an inelastic phenomenon in ion surface interactions and has tremendous important applications in materials analysis. In SIMS [37], the ionized fraction of the sputtered species (known as secondary ions) is detected by a mass spectrometer equipped with appropriate ion collection optics. SIMS is sensitive to all elements in the periodic table, including hydrogen. Among all the surface-analytical tools currently available, dynamic SIMS is the most favoured technique because it offers in-depth (three-

dimensional) information with a combination of highest detection sensitivity (parts-per-billion) and excellent depth-resolution (down to less than 5 nm).

However, these advantages of SIMS are counterbalanced by its strong matrix effect [37, 38] i.e. the ionization probability of a given species varies by several orders of magnitude from one matrix to another, containing that particular species. Consequently, the secondary emission of a given ionic species is greatly affected by the instantaneous local surface chemistry of the sample. Since the ionization probability of a certain species is entirely matrix dependent, the secondary ion yield of that species has no straightforward relationship with the concentration of the species in the host, causing thereby a genuine hindrance to quantification. This phenomenon is known as the matrix effect in SIMS. Compensation of the matrix effect is needed for quantification in SIMS and is possible by several methods such as calibration curve [39], ion implantation standards [40] etc. All these approaches need standards with matrix composition close to that of the unknown sample. Moreover, it is very difficult to make compositional analysis of the interfacial regions using the above techniques. There is another technique known as infinite velocity approach [41], which makes use of the high energy part of the secondary ions that are essentially unaffected by the instantaneous local surface chemistry. The major difficulty in this method is, however, the detection of high-energy secondary ions because of their extremely low count-rates compared to that of low-energy secondary ions.

IV. ELEMENTAL QUANTIFICATION AND MCSN+ SIMS

Irrespective of the mechanism of secondary ion formation, quantification in dynamic SIMS is universally accepted as the conversion of a secondary ion current I± The most widely used technique for quantitative SIMS analysis depends on finding relative sensitivity factors (RSF) for a certain species. In order to determine the sensitivity factors, appropriate reference materials or standards (the term is defined for materials whose composition has been determined by (t) of a given species in a homogeneous target matrix, measured as a function of time t, to a concentration C(z), measured as a function of depth z. Calibration of the depth scale is based on a strictly linear proportionality between the elapsed erosion time and the eroded depth of the sample, considering constant sputtering conditions throughout the measurement and consequently a fixed erosion rate. In reality, however, the linear time-to depth mapping may not be strictly valid as the erosion by ion bombardment introduces smearing of depth information by both target atom relocation and surface topography development. But the major factor that hinders elemental quantification is the matrix effect. However, there exit certain techniques through which one can quantify a species of interest in the host matrix.

The most widely used technique for quantitative SIMS analysis depends on finding relative sensitivity factors (RSF) for a certain species. In order to determine the sensitivity factors, appropriate reference materials or standards (the term is defined for materials whose composition has been determined by independent means, either directly by analytical measurement or indirectly from the method of synthesis) are needed. The accuracy of the quantification obviously cannot be better than that of the standards. However, in developing a suitable standard, the greatest problem encountered is often to get an independent, artifact-free reference method that can be used to calibrate the SIMS method. The principal characteristics of a suitable standard for the determination of sensitivity factors for SIMS are A. The composition should be homogeneous, both laterally and in depth since the sample layer eroded during determination of the intensity ratio may be quite shallow. It is also important to design the materials which allow the accurate measurement of erosion rates and the ion yields in the first few nm of a profile in order to establish the accuracy of the ultra-shallow profiling. B. The composition should not be significantly altered during analysis by the effect of ion bombardment.

There are two simple approaches towards quantification using standards the ion-implanted standards method.

A. Calibration curve method

This method relies on constructing a plot Ix, the intensity of the detected species as a function of Cx, the respective elemental concentration for standards containing the species x with various known concentrations [39, 42]. In order to keep the systematic uncertainties small, the sample to be measured must have a composition close to one of the standards used. The calibration curve of the species x in a matrix can be different from the calibration curve obtained for the same species in another matrix. For the determination of the unknown concentration of a species, the calibration curve is used as an analytical curve, where Cx is considered a function of Ix

B. Implantation standard method

This technique is much more accurate method for quantifying certain species present in a matrix [43,44]. In this method a local standard is prepared by implanting a controlled quantity of the species of interest with a known dose into a sample which should have the stoichiometry identical with that of the host matrix. By measuring the total fluence (dose) of the implanting species and the depth integral of the implant SIMS profile, RSF for the species x in the host sample is determined. The estimated (RSF)x is then used to get the instantaneous concentration of the species in the matrix. The use of implanta-

tion standards for SIMS was first reported by Gittins et. al. [45] and has proven extremely useful for quantitative SIMS analysis of electronic materials. Such standards provide quantitative information on both the local solute concentration and on the distribution of the solute in the structure. One of the great advantages of this method is that the constituent of interest can be implanted directly into the near-surface region of an unknown sample to fabricate an in situ standard. Since the implanted dose is sufficiently small in comparison to the atomic density of the sample, the response characteristics of the sample are not altered because of the presence of the implant. The implanted dose is, therefore, subjected to the same chemical environment as the sample atoms, and the matrix effects should be identical to both. Although quantification in a given matrix can be achieved by using standards with matrix composition as close as possible to the unknown sample, it is very complicated to quantify or even interpret the analysis across interfaces composed of matrices of different nature like metal/semiconductor, metal/polymer, metal/ceramic, etc. Some attempts have been made to correct point by point distortion of a depth profile across an interface due to the matrix effect by using a calibration curve [46, 47]. This calibration curve giving the variation of ion yield with matrix composition was previously established by carefully studying a set of samples with different compositions. There is no doubt that the accuracy of the calibration was seriously limited by the exact evolution of the matrix composition at each point and the linearity of the calibration curve. SIMS analysis under conditions of reduced or no matrix effect is certainly a better way to measure the distribution of elements across interfaces. The matrix effect depends largely on experimental conditions, namely the nature of the primary ion, the incident angle, the detected species and the energy of secondary ions.

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