SIMS for analysis of nanostructures

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Abstract

Secondary ion mass spectrometry (SIMS) has joined the ranks of commonplace analytical tools for nanostructures in ways that would have been difficult to foresee even a decade ago. In particular, improvements in numerical data processing have permitted the use of SIMS in one dimension with uneven surfaces and in reconstructing compositional profiles in two and even three dimensions. These developments offer perhaps the brightest prospects for making SIMS a leading member within the select family of first-line characterization tools for nanoelectronics, nanoparticles, and polycrystalline and composite materials – as well as expanding the science base for tailoring such structures.

Introduction

Ever since secondary ion mass spectrometry (SIMS) originated in the 1970s as a surface analytical tool [1], the fundamental principle of operation has remained the same: ions impinge on a solid that sputter some of the atoms, whose masses are determined by mass spectrometry. The resulting mass spectrum yields a measurement of the composition that is exquisitely sensitive. This concept has spawned a variety of ion sources (electron ionization for gases, surface ionization for Cs, liquid metal). Choice depends upon the required current, usage in pulsed or continuous mode, spot size, and specimen properties. Cs^+ ions often compose the primary incident beam, and provide both sputtering and milling. Yet Cs^+ tends to form complex ions, especially with oxygen; thus many other atomic ions find use including Ar^+ , O^- , O^+ , Ga^+ , and Xe^+ . For the large secondary ion masses characteristic of polymeric and biological specimens, cluster ion beams, such as C_{60}^+ , are employed. Mass identification employs sector, quadrupole, or time-of-flight (TOF) analyzers. Most SIMS instruments can run in either static or dynamic modes. In static mode, the energy and fluence of the primary ion beam are sufficiently low to remove very few of surface atoms, providing minimal invasiveness. Pulsed primary ions with TOF detection permits simultaneous detection of many masses but is slow. Dynamic mode employs higher ion energies and fluxes for continuous compositional profiling over substantial depths. Hybrid methods combine the two modes in alternation, typically with two separate primary ion beams.

Building upon earlier examples [2], several fine book-length reviews of these variants have appeared in recent years providing either a general overview [1] or insights into specific modes of operation [3] or applications [4-5]. Shorter, more focused reviews have also appeared treating materials science [6], organic molecules [7], and soft materials that include polymers [5,

8], biological samples [9-10] and even liquids [10]. However, the application of SIMS to nanostructured surfaces does not appear to have been examined specifically.

SIMS offers no silver bullet for characterization, but rather exists as one useful tool among many. SIMS is most naturally a one dimensional technique, capable of superlative depth resolution (1-2 nm), but more limited lateral resolution no larger than the spot size (50-100 nm) for imaging individual structures in 2-D [11] or 3-D [12]. Moreover, SIMS is most naturally an atomic composition technique, although use for molecular composition is developing in applications focused mainly upon biology [13], polymers [14] and organic chemistry [15].

Despite the limitations, a key development over the past few years has been the integration of SIMS into the family of techniques that provide first-line nanostructural characterization. From basic research to metrology in a manufacturing line, SIMS has joined the ranks of commonplace analytical tools in ways that would have been difficult to foresee even a decade ago.

Methodological Advances

Spatial resolution

Depth

Improvements in depth resolution continue to progress, and now lie somewhat below 1 nm with the use of low incident ion energies < 150 eV [16-17] and extremely smooth surfaces. Under such conditions, however, the sputtering rate drops sufficiently low to impede detection, thereby degrading either mass separation or profiling rates (< 1 nm/min). Certain physical phenomena limit localized depth resolution both near the free surface and in more deeply buried structures. For example, intermixing from the beam-induced collision cascade represents a fundamental constraint [16]. Most progress has resulted from using lower beam energies [18], but as that approach runs out of steam, attention has turned to use of beams of alternate ions or even cluster-ion beams (*e.g.*, C_{60}^+ [19]). Clusters offer reduced penetration depths but introduce other nonlinear effects due to the many-body nature of the sputtering process. Primary ion incorporation and other compound formation are particularly troublesome in the vicinity of the free surface, as the concentration of the impinging ion builds up transiently and affects sputtering yields and intermixing effects in a depth-dependent way.

Absolute depths are typically calibrated by exposure of a reference specimen to the primary beam, followed by *ex situ* measurement of crater depth by atomic force microscopy (AFM) or stylus profilometry [19-21]. If these techniques are applied directly to the specimen of interest, they are applied after the SIMS measurement [5, 22], leading to possible artifacts from embedded Cs, surface reconstruction or specimen oxidation upon removal from UHV conditions [23].

Given these fundamental complications, it is difficult to foresee much further improvement in depth resolution by conventional SIMS. Depth resolutions approaching 0.5 nm may become possible via entirely distinct concepts, such as Tomographic Atomprobe or “zero-energy SIMS.” In the former case, material emission depends upon laser-assisted electric field evaporation, while the latter relies upon electron-beam induced etching in the presence of a reactive gas such as XeF_2 [24]. However, these methods are restricted to particularly favorable matrices and analytes, and forego the generality of SIMS to many materials.

Lateral & 3D

Improvements in primary beam focusing and secondary ion detection has pushed lateral resolution as low as 50 nm [25-26], permitting direct imaging of elemental segregation at grain boundaries in certain polycrystalline solids [11, 27]. Figure 1 shows an example. Further resolution may be obtained by matching the primary beam with one of the analytes and detecting secondary cluster ions of this species. Such “self-focusing” SIMS promises lateral resolution as low as 20 nm but is still in its infancy [28].

Figure 1: (Color Online) Polycrystalline CdTe after CdCl₂ treatment. Cl⁻ (pink) and Te⁻ (blue) demonstrate atomic chloride segregation at grain boundaries. Image size: 26 * 26 μm using a 256*256 pixel scan. Reprinted with permission from Ref [11], Figure 2C. Copyright 2014 John Wiley and Sons.

Data analysis by numerical methods has advanced considerably in recent years to aid in 2D and 3D compositional analysis. Such methods rely upon separate data, often collected *in situ*, regarding sputtering rate [29] and surface topography [12,30]. Figure 2 shows an example approach that integrates SIMS with scanning probe microscopy (SPM).

Figure 2: 3D SIMS in the presence of three elements and surface roughness. (a) Standard SIMS 3D mapping: poor accuracy due to inappropriate assumption of flatness. (b) Successive SIMS and SPM/AFM images, and software reconstruction, account for sample topography and its evolution during sputtering. Reprinted with permission from Ref [12], Figure 1. Copyright 2012 AIP Publishing LLC.

Concentration

Despite the exquisite sensitivity of SIMS on a relative scale into the parts per billion range, absolute concentration measurements remain a multifaceted problem dependent on beam type and sample composition. The ionization likelihood for an analyte varies with beam type and energy. Formation of ion complexes between the analyte and matrix can induce deviations of ion yields by orders of magnitude from the “neat” analyte [31]. When the analyte is not dilute, sputtering yields depend upon concentration relative to the matrix. Incorporation of the primary ion into the intermixed layer affects composition resolution further, especially if a new compound (such as an oxide) forms. Absolute concentration measurements therefore require standard samples of known concentrations, with numerical principal component analysis [20, 32-33] finding use for complex compositions. Other externally supplied information such as natural isotopic abundances may also be employed [26]. Such requirements have remained constant throughout the years and are unlikely to change in the future.

Applications

Most of the recent extensions of SIMS into new domains of application have resulted from improvements in lateral and depth resolution afforded by advances in commercial instrumentation. Individual research laboratories typically contribute to improved protocols for specimen preparation, numerical data analysis and interpretation, and integration of SIMS with other tools [34] for investigation of ever-smaller structures.

SIMS is an intrinsically destructive technique. Its applications therefore remain mostly in the domain of research and development rather than manufacturing. The laboratory setting focuses on maximal spatial resolution and accuracy in absolute concentration measurements, whereas the fabrication environment seeks mainly low-cost methods that provide rapid, statistically relevant data for yield improvement and process control. Despite its complexity, SIMS is being increasingly viewed as a “lab to fab” technique for electronic devices, especially with the possibility of self-focusing. Commercial instruments for manufacturing have become available for near-line metrology [35].

Irrespective of application, SIMS has cemented its place as a favorable compositional characterization tool due to the robust nature of operation and straightforward analysis. The closest competition to SIMS in 2-D or 3-D combines a surface technique, such as X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES), with ion milling for depth profiling [36]. XPS can achieve comparable lateral resolution and has the dual advantages of sensitivity to chemical valence state and use of X-rays as a less intrusive probe than ions. This gentler perturbation avoids the collision cascades that degrade near surface depth resolution for SIMS as discussed above. However, XPS has difficulty detecting lighter elements (especially hydrogen), and the requirement of ion milling for depth profiling reintroduces the same collisional mixing and preferential milling problems that SIMS suffers.

Nanoelectronics

The two greatest contributions to SIMS for micro- and nanoelectronics have probably been a) the integration of SIMS as part of the family of go-tool characterization tools, and b) the improvement in software packages for reconstructing SIMS data into profiles in 2D and 3D. Much work incorporated SIMS into multifaceted examinations with complimentary techniques

including scanning probe microscopies [12, 29, 37], Hall effect measurements [21] and resistance-based microscopies [38], and high-resolution X-ray diffraction (XRD) [29, 37]. Most complimentary techniques are compatible with the high vacuum required by SIMS, making *in situ* monitoring possible.

The sub-nm depth resolution of SIMS in some cases is quite adequate for many purposes, although the surface unevenness of actual devices poses difficult problems. Lateral resolution of 50 nm is typically too large for imaging individual nanoelectronic devices, and this limitation is unlikely to be surmounted soon. Applications requiring such resolution often turn to highly specialized atomic probe techniques [39], sometimes as a complement to SIMS.

Nanoparticles

Direct characterization of nanoparticles by SIMS is becoming more common, including not only particles of a single nominal composition [40] but also core-shell structures [19] and organic-coated particles [35]. However, possible artifacts are significant. Sputtering of nanoparticles often occurs at rates different from those of thin films or bulk materials, so depth information may be unreliable. Needs for complimentary composition information often turn to *in situ* XPS [40-42].

Even when very low primary ion energies are employed, melting may occur within the particle due to inadequate heat transfer to its substrate [19]. Such melting further complicates the interpretation of depth profiles. Complimentary topological information is often obtained using SEM [41] and TEM [25, 41] for a more complete image of the sample.

Grain structure and spatial composition in polycrystalline and composite materials

Two-dimensional SIMS measurements have found an important niche in analysis of polycrystalline materials, including compositional and isotopic analysis of minerals for geochemistry and cosmochemistry [18], corrosion monitoring of alloys for nuclear reactors [43-44], and other applications [19]. Elemental segregation to grain boundaries can be quantified even when the width of the grain boundary itself is substantially less than the ion beam's spot size [11, 45]. Application to a metal permits polishing that facilitates accuracy. The procedure assumes that sputter yields and ionization probabilities are identical from a scanned area lying entirely within in a bulk grain and an area containing a grain boundary. The total volume of material contributing to the analysis is much larger than the volume of grain boundary. Hence, the matrix including and excluding the boundary is largely identical. Similar to nanoparticles, complimentary techniques for both morphology and composition data are common often including (XPS) [23, 42], atomic force microscopy [22-23], Auger electron spectroscopy [23], energy-dispersive X-ray spectroscopy [43, 46], scanning electron microscopy (SEM) [43-44] and transmission electron microscopy (TEM) [44, 46].

In a related vein, direct mapping of elemental segregation in glasses has also been demonstrated [46], again facilitated by the smooth surfaces. Soil and sediment particles can be examined by embedding them in a polymeric resin, and polishing the composite [42]. This procedure eliminates topographical variations in local sputtering efficiencies by losing a majority of the outer surface of the particle.

Science base for nanotechnology

SIMS has played a linchpin role in discovering new phenomena that have direct relevance for fabrication of nanostructures. One example is atomic-scale defect engineering,

which involves manipulating the type, concentration, spatial distribution, or mobility of defects within a crystalline solid [47]. Such defects mediate dopant diffusion in semiconductors used for nanoelectronic devices and affect the performance of semiconductor-based sensors, catalysts, photo-active devices, and photovoltaic cells. Example methods for achieving such control include specially designed heating protocols (time, maximum temperature, heating and cooling rates) and introduction of foreign atoms. A more recent approach includes controlling the chemical state of nearby free surfaces, which is important at the nanoscale where surface-to-volume ratios are high. The surface injects or annihilates point defects in Si [48], TiO₂ [49-50], and ZnO [P Gorai *et al.*, submitted] by preferential interaction with dangling bonds or related sites, in ways that are mediated by surface electric fields [51-53]. The effects of this method can be seen in Figure 3. Recently, the ability to absorb oxygen via a mobile defect has enabled a better understanding of the performance of TiO₂ as an oxygen scavenging material [54]. Another such method is photostimulation, which can exert nonthermal effects by changing the charge state of point defects within the semiconductor [55-57] or at a surface or interface [58]. This phenomenon is relevant to nanoscale device fabrication by rapid thermal processing. These experiments relied heavily on self-diffusion measurements made by depth profiling of isotopic heterostructures or isotopic exchange with an ambient gas. SIMS depth profiling, combined with continuum modeling of defect-mediated diffusion [59-60], were indispensable in uncovering the underlying defect physics. Depth scales below 10 nm were often entailed [53].

Figure 3: Depth profile of ¹⁸O near a rutile TiO₂(110) surface. The single crystal is annealed in ¹⁸O₂ gas to stimulate oxygen exchange between the gas and solid. For very clean surfaces, O is injected in interstitial form charged (-2). The built-in electric field due to surface band bending opposes diffusive motion of the interstitials, which gives them more time to kick into the lattice and pile up over time. See Refs [50-52] for details.

Conclusion

Fundamental physical limits have been largely reached for depth resolution, but improvements in both spot sizes and numerical data processing continue to offer prospects for advancing use of SIMS in 1-D with uneven surfaces and in reconstructing compositional profiles in 2D and 3D. These developments, together with refinement of protocols for minimizing sputtering yield variations from local topography offer perhaps the brightest prospects for confirming SIMS as a leading member within the family of first-line characterization tools.

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