

Nanocharacterization Using Secondary Ion Mass Spectrometry (SIMS)

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ABSTRACT

Secondary Ion Mass Spectrometry (SIMS) using ultra-low energy beams (<1keV) gives the capability to measure structures within films as thin as 1nm. By measuring SiO₂ calibration films of known thickness and extrapolating back to zero thickness, we can calculate the ion mixing depth of the SIMS measurements. These data show that SIMS can achieve depth resolution of less than 1nm using beams of 700-300eV. By using an inorganic elemental tag, an isotopic tag or staining, low energy depth profiling can also discern the structure of planar organic films. We give examples of Zn-doped layers of tetraphenylporphyrin (TPP) and a self-ordered polystyrene/polybutadiene copolymer film stained using OsO₄. Standard SIMS measurements have also been carried out on doped Si nanowires to measure boron doping levels.

Keywords: sims, gate oxide, copolymer, nanowires

1 INTRODUCTION

The technique of secondary ion mass spectrometry (SIMS) is one of the few tools having the requisite resolution to characterize nanomaterials. Because nanometer scale resolution is available only in the depth dimension, SIMS has not been widely applied to analysis of nanomaterials. It is the purpose of this article to show that experiments can be devised in ways that take advantage of SIMS depth resolution to allow characterization of several types of nanostructured materials.

The SIMS technique consists of bombarding a solid with an energetic ion beam and detecting the ions emitted from the surface using a mass spectrometer [1]. It has been applied most widely for trace element analysis of semiconductors and other materials used in the manufacture of microelectronics, however it can be used to measure any solid material. SIMS is most often used to acquire depth resolved information, presented as a plot of ion intensity or concentration versus depth, but can also be used to measure the bulk concentration of trace impurities in a solid. It is the combination of sensitivity and high depth resolution that makes SIMS valuable for characterizing nanostructures.

2 SIMS DEPTH RESOLUTION

We first need to demonstrate that SIMS has nanometer scale resolution. In recent years nanometer scale SiO₂ layers are being used as gate dielectrics in MOS capacitors [2]. These oxides are now on the order of 2nm thick and

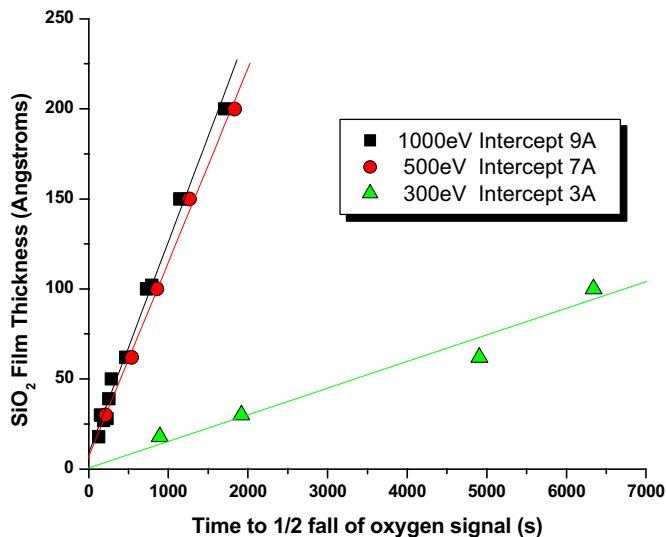


Figure 1. Measurement of the time required to sputter through oxide films versus film thickness. All measurements done at an incidence angle of 75 degrees from normal.

must be tightly controlled in uniformity. Because they are formed on a highly polished Si wafers they provide ideal calibration samples to measure the resolution of the SIMS technique. By plotting the time required to sputter through the films against their known thickness, we can extrapolate back to zero time to calculate the thickness of the ion mixed layer induced by ion bombardment. [3]. Figure 1 shows a series of measurements on oxide films of various thickness acquired using Cs ion bombardment at three impact energies. Extrapolating these trends back to zero time indicates ion mixing depths of 0.9nm for 1keV, 0.7nm for 500eV and 0.3nm for 300eV bombardment energies. The mixing depth is usually considered equivalent to the depth resolution of the technique.

Thus we can demonstrate that SIMS has sub-nanometer depth resolution for oxide films on well-controlled polished Si wafers. This level of depth resolution is available to measure any solid layered structure, providing the layering is planar over the area of analysis and the substrate is flat. An example of a high-resolution measurement is given in Figure 2. This depth profile shows a 3nm thick SiO₂ film that has been treated to introduce nitrogen into the film. The high resolution of the measurement allows us to see that nitrogen is accumulated at both the surface of the film and the substrate interface.

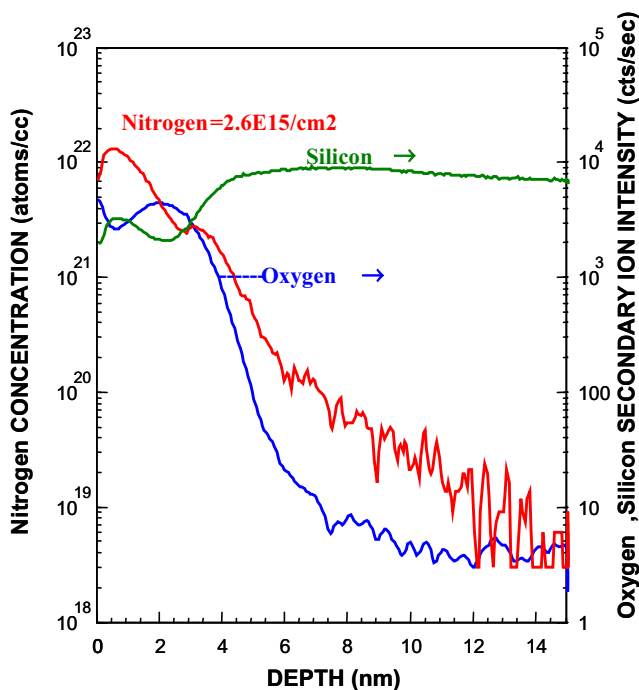


Figure 2. SIMS depth profile of a nitrided SiO₂ film.

3 DEPTH PROFILING LAYERED POLYMER STRUCTURES

Nanostructured materials are being formed from layered polymer films and copolymer blends because these materials can be tailored to form various structures depending on the molecular weight of the polymers and percentage of each in a blend [4]. In order to use SIMS to characterize such materials we must have way to distinguish the different compounds and we must have a planar structure. There are three options to tag the components of a polymer structure such that SIMS can distinguish them: inorganic tagging, staining and isotopic tagging. Only the first two techniques are discussed here as many isotopic tagging experiments have been used to show details of copolymer blends [5].

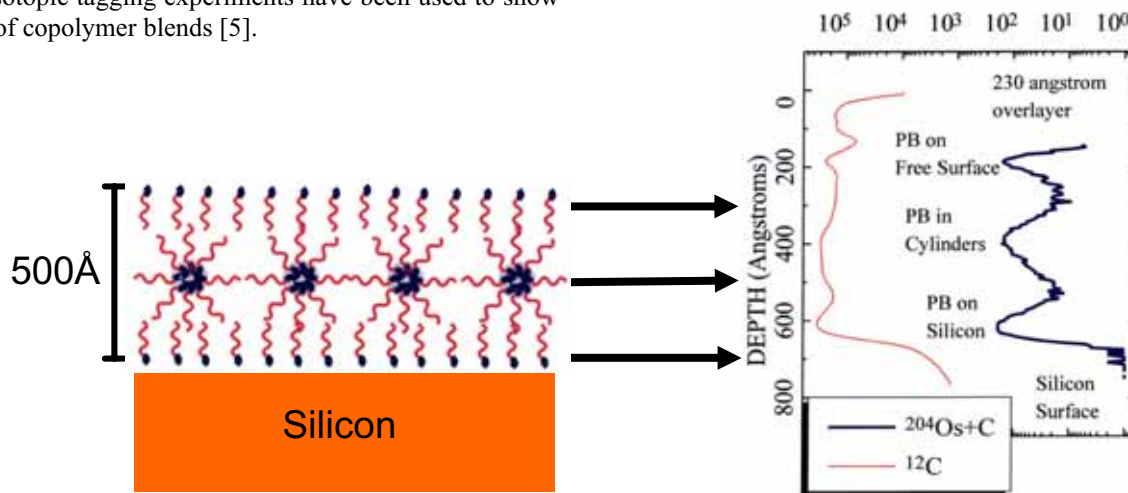


Figure 4. Cartoon structure of a PS/PB copolymer layer and corresponding SIMS depth profile of a stained film.

3.1 Depth Profiling Using an Inorganic Tag

One method by which SIMS can discern two organic materials in a layered structure is to tag one with an inorganic element. Figure 3 gives an example of a sample in which alternating layers of 5,10,15,20 tetraphenylporphyrin have been deposited on a Si wafer substrate [6]. Layers doped with Zn have been deposited between undoped layers by the technique of atomic layer epitaxy.

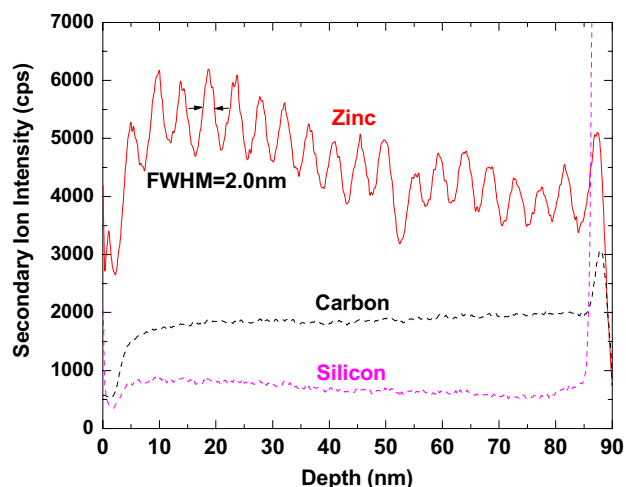


Figure 3. Depth profile of TPP:Zn/TPP layered sample by SIMS.

This profile allows us to demonstrate that layers of about 2nm thickness were deposited, count the number of layers and state that the layer thickness is quite uniform through the deposition. Many other elemental tags could probably be used in this application successfully, such as F or S, depending on the interaction with the polymers used in the structure. A flat highly polished substrate is essential.

3.2 Delineation of Structure using Staining

Copolymer blends are being investigated as a way to form regularly patterned templates for such uses as nanolithography [7]. Copolymers consist of a mixture of two dissimilar polymers that spontaneously order into nanometer scale structures at equilibrium. Changing the relative proportion of the polymers yields different exsolution structures, ranging from lamellae to ordered spheres to a complex three-dimensional lattice [8]. SIMS can discern the structure of the exsolved films because of its high depth resolution. Many polymers are compositionally quite similar, however, so it is difficult or impossible to detect the individual polymers on the basis of elemental signals. It is possible to selectively tag doubly bonded polymers using standard osmium tetroxide staining that is widely used for staining biological structures. By monitoring the Os signal, a SIMS depth profile will show the location of the doubly bonded polymer.

Figure 4 gives an example of a copolymer film that consists of polystyrene (PS) and polybutadiene (PB) deposited on a Si wafer. After annealing the film consists of cylindrical polybutadiene agglomerations surrounded by polystyrene. The overall structure of the film was confirmed by plan view TEM, however the existence of the top and bottom PS/PB layers is not evident from TEM examination. A depth profile of an OsO_4 stained film is shown on the right side of Figure 3. Because PB contains doubly bonded C and PS does not, the OsO_4 should selectively stain the PB. The Os+C signal clearly shows concentrations of Os at the top and bottom of the film, corresponding to the additional layers, as well as the broader peak in the center of the film that corresponds to the PB cylinders. Thus SIMS was able to confirm details of a three layer film that were not available in TEM.

4 MEASURING DOPING IN Si NANOWIRES

The formation of Si nanowires is being investigated as a route to further miniaturizing semiconductor devices and to examine Si properties in confined systems [9]. One method of forming nanowires uses an alumina template with a gas-phase catalyzed reaction [10]. Regularly spaced pores in the alumina film are the template for growth of the nanowires, which extend upward from the surface of the film. The nanowires form a dense partially oriented aggregate on the surface of the template (Figure 5). This growth method produces wires that are approximately 80nm in diameter and up to 30 micrometers long. Both B and P doped wires have been produced but only the B-doped wires are discussed here.

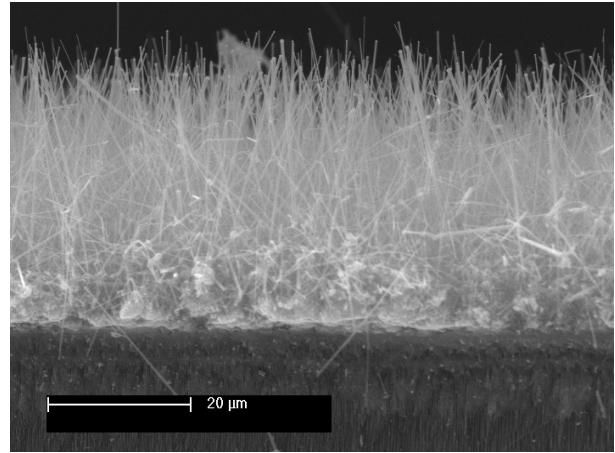


Figure 5. SEM image of Si nanowires on alumina substrate.

SIMS measurements are the standard method to determine the concentration of dopants (boron in this case) in silicon; however it was not clear if standard SIMS techniques could be used to analyze the nanowires. Initially we simply analyzed the aggregate of Si wires as in a standard depth profile and quantified the boron signal as in a typical profile. The results of SIMS measurements of 5 different nanowire arrays grown with different dopant gas flows are shown in Figure 6. The good correlation between gas composition and doping measured by SIMS indicates that changes in the gas composition change doping within the wires and that we appear to be measuring doping of the wires well. Four point probe measurements of individual wires give resistivities that correlate well with the SIMS measurements, although they do not provide absolute resistance measurements to allow calculation of B doping. The minimum B level measured here, about 1×10^{18} atoms/cm³ is the minimum measurement limit due to a background signal from B on the surface of the wires and the alumina substrate. Similar measurements have been performed on phosphorus-doped Si nanowires.

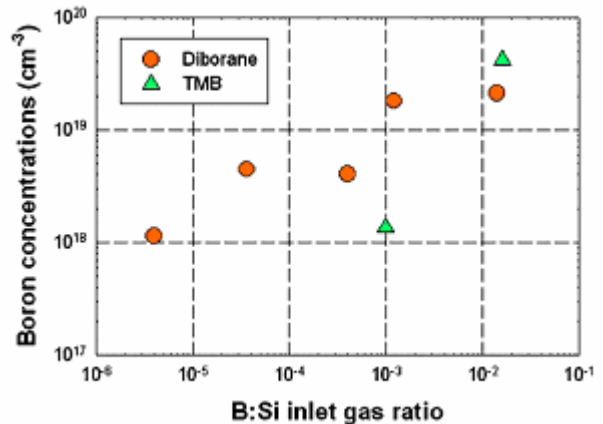


Figure 6. SIMS measurements of B doping in Si nanowire aggregates grown with two different gas sources. TMB=trimethylboron.

5 CONCLUSIONS

The SIMS technique has demonstrated depth resolution of better than 1nm when using beam energies less than 1keV and a high incidence angle. These conditions have allowed us to analyze 2nm thick oxynitride films, films containing 2nm doped organic films and a self patterned polystyrene/polybutadiene block copolymer film 50nm thick. In addition standard SIMS measurements have been used to detect B and P doping variations in Si nanowires. Many other types of nanostructured materials can be analyzed by SIMS, depending on the inventiveness of the investigator. To obtain the best resolution for depth profiling layered films it is imperative that flat highly polished substrates are used.

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