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ANALYTICAL APPLICATIONS OF NEUTRON DEPTH PROFILING

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Using a low-energy neutron beam as an isotopic probe, neutron depth profiling (NDP) provides quantitative depth profiles in nearly all solid matrix materials. Several of the light elements, such as He, Li, B, and N can be nondestructively analyzed by NDP. The information obtained using NDP is difficult if not impossible to determine by non-nuclear techniques. As a result, NDP is used collaboratively with techniques such as SIMS, RBS, FTIR, PGAA, and AES. Profiles measured by NDP are given for semiconductor and optical processing materials, and light weight alloys. Improvements in the technique are discussed with emphasis on the use of intense cold neutron beams.

Introduction

Neutron absorption reactions that produce prompt energetic charged particles are being used to quantitatively profile in depth a number of technologically important elements. In just the last decade over ten nuclear facilities world-wide have employed the technique in the investigation of the near-surface region of a diverse selection of materials. Other facilities are being developed in the United States to commercially exploit the procedure for nearly routine industrial analysis of materials /1/. This technique, which we refer to as neutron depth profiling (NDP), has evolved into an effective research tool for the determination of helium, lithium, boron, nitrogen and a limited number of the other light elements. Ziegler et al. /2/ first used NDP to determine implantation range and profile parameters of boron in semiconductor silicon and the technique continues to be extensively

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used for these measurements /3/. Biersack and coworkers /4,5/ have led the community in the development of NDP by introducing innovative approaches in its use for basic research. In this paper analytical applications of NDP are presented for several new technologically significant materials investigated at the National Bureau of Standards 20 megawatt research reactor and several proposed enhancements to the technique.

Technique Description

The neutron depth profiling technique is fundamentally simple. A sample volume is uniformly illuminated with low energy neutrons. Upon the absorption of a neutron certain nuclides react by the isotropic emission of alpha particles or protons and the diametrically emitted recoil nucleus. Each particle is emitted with a characteristic energy determined by the mass balance of the reaction. Only helium, lithium, boron, and nitrogen have a stable isotope with a thermal neutron cross section greater than one barn for charged particle emission. Long-lived radioactive isotopes of beryllium and of sodium have cross sections in the tens-of-thousands of barns. The count rate and residual energy are simultaneously measured from all depths for the particle species emitted during the reactions in the direction of a surface barrier detector or electrostatic analyzer. The resultant spectrum is ultimately deconvoluted into an isotopic concentration versus depth profile. Detailed descriptions of other reactions, sensitivities and NDP facilities are described in detail elsewhere /6,7/.

By using an intense, well-collimated beam of low-energy neutrons (≈0.025 eV) to induce the charged particle reactions, NDP can nondestructively probe the first few micrometers of sample depth. Neutrons are characteristically less intrusive toward the constituents of a material than other analytical profiling instruments that use energetic beams of charged particles, electrons or intense beams of photons. A gamma-ray component carried with the neutron beam can, however, induce damage in energy sensitive materials, for example polymers that often become brittle upon irradiation with photons. The useful range of depth investigated in a single NDP analysis will ultimately be limited by two parameters: i) the rate energetic particles lose energy in passing through the material, which is a function of the particle, the current energy of the particle and the material /8/ and ii) the initial kinetic energy of the particles produced in the nuclear reactions /9/. Typical resolutions of 10 to 50 nanometers are obtained, but again this is highly dependent upon the depth at which the feature is being resolved. Depths of 1 to 10 microns are common profiling ranges for most materials.

An important point to be emphasized is that NDP measures only a particular isotope of an element and not the total elemental concentration. Elements such as lithium are variable in isotopic abundance and therefore NDP is only indicative of the total concentration when the isotopic composition is known.

Applications

Semiconductors

The most frequent application of NDP has been for the study of silicon semiconductors. Downing et al. /3/ have briefly reviewed the first NDP experiment by Ziegler et al. /2/ and nearly 60 subsequently published accounts where NDP was used in the study of semiconductor-related materials.

NDP is quantitative, nondestructive and has few interferences in silicon based materials. As a result it is often used for calibrating other techniques and verifying the profiles they generate. Instrumental techniques such as secondary ion mass spectrometry (SIMS), Fourier transform infrared spectrometry (FTIR), and Auger emission spectrometry (AES) have greater sensitivity than NDP in most applications and better resolution in some matrices, but each of the other techniques is subject to highly interactive chemically and electronically induced artifacts. On the other hand, NDP is primarily subject to the less interactive nuclear effects. Rutherford backscattering (RBS) and neutron depth profiling, which both rely upon interactions with the nucleus, complement each other in 'nondestructive' profiling capabilities. RBS measures heavy atoms in light matrices but is of limited use for light elements in heavy matrices. NDP, conversely, profiles a limited group of light elements in most solids.

An example of the synergism between NDP and SIMS is the boron profile measurement in borophosphosilicate glass (BPSG). The presence of phosphorous will alter the boron signal detected during a SIMS analysis of the glass passivation layer

on a semiconductor device. This can potentially yield wrong values for both the total boron concentration and its depth profile /10/. NDP can accurately establish the total boron concentration and measure the depth profile in a straightforward manner. The phosphorous atoms simply contribute to the total stopping power of the material in the NDP profile measurement. Using NDP as a reference technique, the more highly resolved SIMS profile can be normalized to the concentration determined by NDP and compared with the NDP profile to identify any spectral artifacts.

Surface charging causes variation in the ion yield and may cause ion diffusion during SIMS analysis. This is especially evident at interfacial boundaries between SiO_2 and Si. Figure 1 demonstrates the use of NDP in identifying

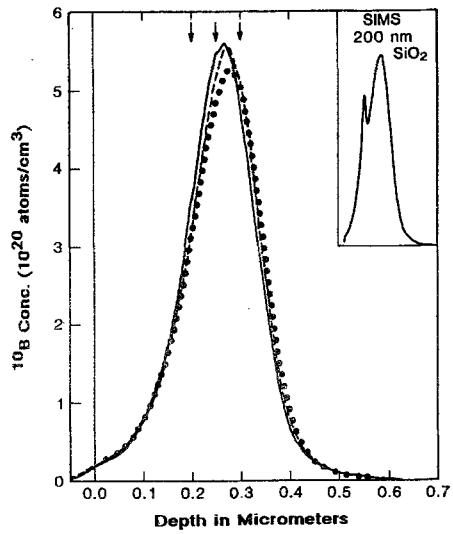

Fig. 1. Boron-10 concentration profile determined by NDP for 1×10^{16} atoms $\cdot$ cm^{-2}, 70 keV implants through three different thicknesses of SiO_2. Arrows at the top indicate positions of the SiO_2/Si interface; — implant through 200 nanometers of SiO_2; – – implant through 250 nanometers of SiO_2, ○ implant through 300 nanometers of SiO_2. Insert shows boron profile with artifact peak at the interface obtained by SIMS for the 200 nanometer specimen

instrumental artifacts and for verifying the existence of concentration variations at the interface of insulating and semiconducting materials /11,12/.

By using thin borosilicate glass films of various concentrations deposited on boron-free silicon wafers, cross calibration standards have been produced with NDP. The standards can be used repeatedly for prompt gamma activation analysis (PGAA), laser RAMAN, FTIR and NDP. If a small quantity of the material is sacrificed, then SIMS can also use the cross calibrated materials. In addition, boron-10 has been implanted with a range of doses and energies into silicon wafers and analyzed by NDP. In this way a multi-technique standard is generated that can be analyzed by NDP for both depth and concentration.

Some care must be exercised in expressing concentration with respect to depth for materials which have been sputter deposited or grown in multiple layers, such as some metallic glasses or semiconductor materials. It has been shown that a density gradient can exist starting from the substrate through the first one-half micrometer of deposited material /13/. This makes assigning a linear depth scale difficult for the nondestructive techniques such as NDP and RBS and directly affects the conversion of concentration units from atoms/cm^2 to atoms/cm^3. When NDP and RBS profiles are expressed in linear dimensions the error in scale is directly proportional to the error in the density.

Surface Modification

NDP has been used to referee the determination of nitrogen concentrations between the targeted implantation dose and AES measurements. The AES technique can provide useful chemical information on the bonding of nitrogen in materials such as tooling steels, however it is unpredictably biased when determining the elemental concentration /14/. Figure 2 shows an NDP determination of nitrogen implanted in a WC-Co alloy /15/ which, when combined with information from a sputtering-AES analysis, provides a more accurate description of the near-surface composition and properties of the material.

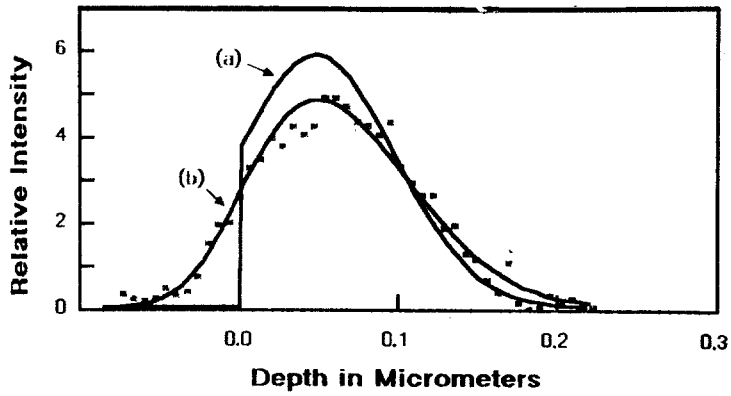

Fig. 2. Nitrogen-14 intensity profile determined by NDP for $5 \cdot 10^{17}$ atoms $\cdot$ cm^{-2} implanted at 90 keV into a WC–Co alloy; ■ measured data, curve a – deconvoluted profile, curve b – profile convoluted by the total energy resolution function

Both figures 2 and 3 compare the as-measured NDP energy profiles to the deconvoluted nitrogen depth profiles. Maki et al. /16/ used an iterative deconvolution method to obtain the best estimate of the actual nitrogen profile. The method convolutes an assumed depth profile according to a total energy resolution function. The convoluted profile is then

compared to the as-measured profile whereby a goodness of fit is determined by a Chi-square value. The assumed profile is iteratively adjusted to minimize Chi-square. Once Chi-square has been minimized, the assumed profile represents the deconvoluted depth profile.

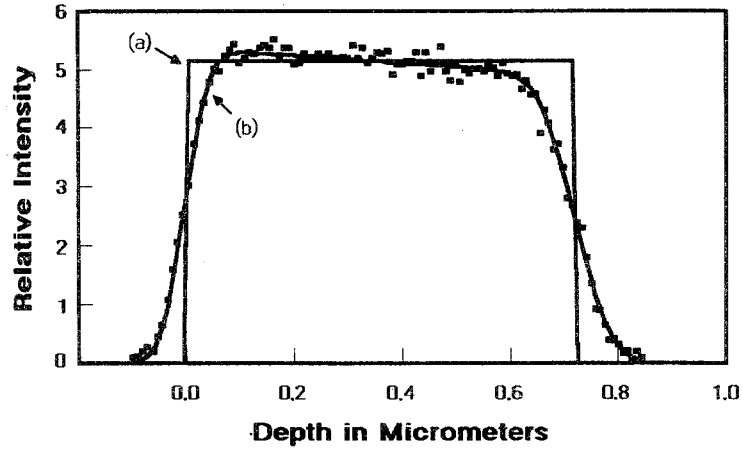

Fig. 3. Nitrogen-14 intensity profile determined by NDP for a TiN film on a metal substrate, ▪ measured data, curve a – deconvoluted profile, curve b – profile convoluted by the total energy resolution function

Optical Wave Guides and Optical Signal Processing Materials

Titanium nitride is used as an optical wave guide material or in other applications as a cosmetic and protective surface coating. NDP is used to analyze methods of TiN deposition /17/ for uniformity of nitrogen distribution and for total film thickness. The nitrogen profile given in figure 3 was determined using NDP for a TiN film deposited with a chemical reactor. By varying reactant parameters such as the oxygen pressure during film deposition, properties of the material can be adapted for a particular function.

Boron is implanted in HgCdTe for the production of infrared detectors. NDP can be used in the analysis of these materials /18,19/ but with some difficulty. Cadmium is a strong prompt emitter of energetic photons and electrons.

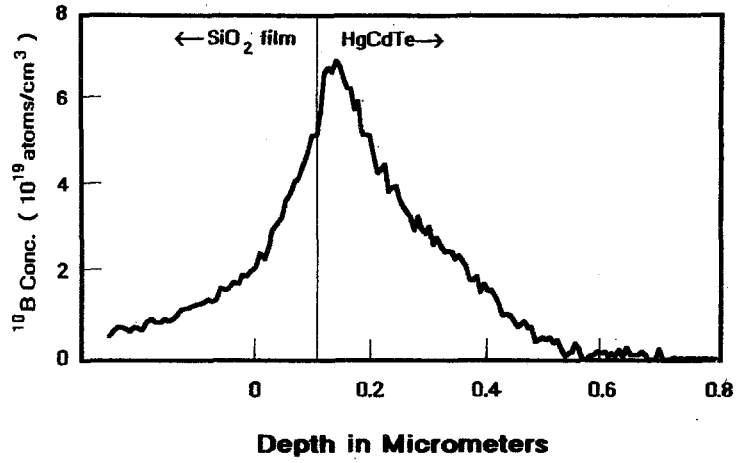

Fig. 4. Boron-10 concentration profile determined by NDP for a implant of $1 \cdot 10^{15}$ atoms $\cdot$ cm^{-2} at 40 keV and then at 100 keV, both through 100 nanometers of SiO_2 on HgCdTe. Solid vertical line indicates depth of SiO_2/HgCdTe interface. Spectrum not corrected for system resolution

These generate background noise in silicon surface barrier detectors which interferes with the measurement of the alpha spectrum of boron. Fink et al. have devised electronic methods to reduce the interference /5/. Figure 4 is a profile obtained with NDP depicting the boron concentration gradient through the SiO_2/HgCdTe interface of a infrared detector /20/.

Lithium and boron are common elements in optical wave guide and fiber optic materials. NDP is used to profile these elements at the near-surface in search of concentration gradients. For instance when coupling two optical fibers, the index of refraction should be as nearly matched as possible in the adjoining sections to maximize the signal transmission.

The material is typically a nonconducting glass, therefore NDP is often the method of analysis chosen because of the relatively few interferences encountered. Leaching of boron from cut surfaces is known to occur when some coolants are used on the sample /21/.

Alloys

Boron and lithium are widely used in the production of modern alloys and metallic glasses. NDP has been used by Nagy et al. /22/ to study boron in metallic glasses. They were able to see variations in concentration of boron between the front and back sides of the ribbon as well as concentration gradients. Many of the NDP facilities have been used to study implantation ranges, stopping powers and profiles of light elements, particularly helium, in pure metals /4,23-35/. Downing et al. have studied the diffusion of bismuth atoms through the surface of a tin substrate using SIMS and a variation of NDP /36/.

Lithium is used as a major constituent in several aluminum alloys to produce lighter materials for applications such as aircraft construction. Because of localized sample charging which causes migration of lithium atoms, Al-Li alloys are difficult to analyze by non-nuclear methods. NDP can provide quantitative depth profiles with minimal intrusion into the sample. This allows a sample to be profiled, returned for further processing, and then analyzed again by NDP or in some cases by other techniques.

Figure 5 is an example of a lithium profile by NDP through the first few micrometers of an Al-Li alloy. An enrichment of lithium, most probably existing as an oxide, can

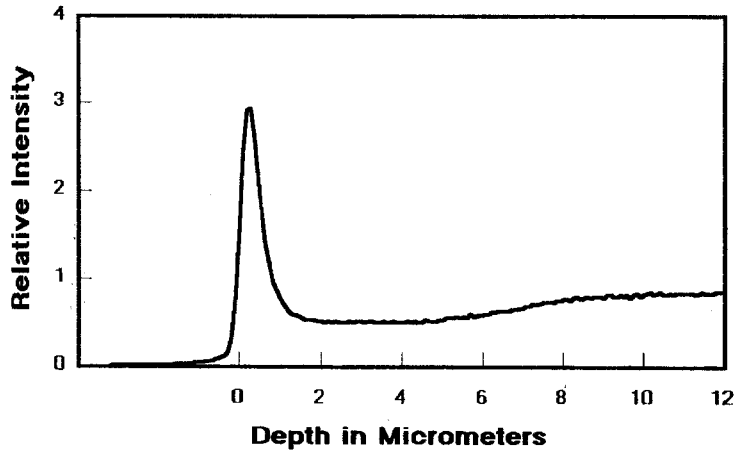

Fig. 5. Lithium-6 intensity profile as determined by NDP for an aluminium-lithium alloy. Spectrum not corrected for system resolution

be seen at the surface of the sample. The lithium observed at the surface of the sample appears to have been leached from the region of depth between 1.5 and 7 micrometers. The lithium concentration of the bulk alloy can be seen beyond the depth of 11 micrometers. The surface enrichment of lithium accounts for the amount of lithium lost from the region of depletion. The profile was obtained using the 2.7 MeV triton. A higher resolution profile could be measured using the 2.1 MeV alpha particle emitted in the same reaction, however it would produce a profile only to a depth of 6 micrometers. The alpha energy spectrum is somewhat more difficult to quantitatively interpret as it appears in with the low-energy portion of the triton spectrum.

Trends in NDP

A cold neutron source and guide hall are being designed for the NBS research reactor. Biersack et al. /5/ have shown the advantages of using high intensity cold neutron beams for NDP analysis at the Institute of Laue-Langevin. A tightly focused beam of cold neutrons produced with a neutron mirror will be dedicated to PGAA - NDP measurements at the proposed NBS facility. It is calculated that 10^{10} n/sec will be focused on an area of less than 1 cm^2 in this facility. Besides the gain in intensity, the detection limit will improve with the increased neutron adsorption cross section of nuclides for lower-energy neutrons. The greater signal intensity will make practical the use of multiple off-angle detectors for improved resolving capabilities and for position sensitive particle detectors /37/. Other elements will be profiled which are presently below the practical detection limit of the technique. Two- and three- dimensional profiling by NDP is a goal of the NBS facility for use in mapping features of microelectronic devices and the grain boundaries of materials. Also, it should be possible to monitor diffusion profiles in a reasonable period of time without having to remove the sample from the target chamber.

Table 1
NDP applications

Isotopic Quantification
Elemental Profiles
Film Thickness Measurements
Instrument Cross Calibration
Interfacial Profiles
Diffusion/Release Analysis
Implantation Ranges
Stopping Power Parameters
Crystal Channeling/Blocking Studies

Table 1 summarizes some of the current applications for which NDP is used. Although spread of the technique is hindered by the limited availability of high quality, intense neutron beams, the number of NDP facilities continues to grow. This growth is not due only to the basic measurement capabilities of NDP but also due to the synergetic capabilities of the technique and the technological importance of the elements that NDP can profile. With time, basic features of the NDP technique are being improved upon by incorporating new approaches, improved detectors and electronics, and better overall neutron facilities.

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