DEVELOPMENT OF THREE NEW STANDARD REFERENCE MATERIALS

The chemical composition of materials critically determines their uses in commerce. Chemical analysis is a large endeavor in industry, and depends on the availability of materials with well-known compositions to develop and validate analytical procedures and laboratories. NIST Standard Reference Materials (SRMs) are the most important such materials in the marketplace. Nuclear analytical methods have been a crucial contributor to the certification of SRMs for thirty years, because of their high sensitivity and specificity, and their freedom from chemical interferences. In addition to the continuing production and characterization of traditional Standard Reference Materials, three new approaches are underway to satisfy critical measurement needs, using the Analytical Chemistry facilities at the NCNR.

Air particulate matter. Investigations into the amounts and composition of particulate material in air are currently carried out in virtually every country. The investigations in the United States are pointing at particularly high risk factors associated with the fine fraction (PM2.5, which is smaller than 2.5 µm aerodynamic diameter) of aerosols. The primary techniques for trace element analysis are based on nuclear physics principles (PIXE, XRF, NAA, etc.), due to their suitability for multicomponent determinations on the small sample sizes that are represented. However, few appropriate quality assurance materials are available to support this work. To assist in effective measurement and control of PM2.5 aerosols in an economically sustainable way, NIST is developing this new class of SRMs.

We have collected air particulate matter corresponding to the PM2.5 fraction in Baltimore, Maryland at an established EPA monitoring site. The aerosol is removed by ultrasonication from the Teflon membrane filters and suspended in water. Individual filters are prepared by filtering aliquots of the suspension through 47 mm diameter polycarbonate filter membranes with 0.4 µm pore size to form the SRM units. Elemental concentrations in this SRM will be certified using a variety of nuclear- and non-nuclear- based analytical techniques.

Hydrogen in titanium alloy. Hydrogen causes embrittlement of many metals, and the industry-standard analytical methods need same-matrix standards to calibrate their instruments. To meet this need we are currently preparing a new SRM by direct reaction of a titanium alloy with measured amounts of hydrogen and using cold-neutron PGAA to verify the doping level.

A procedure has been demonstrated for producing certified reference materials of titanium alloy (6% Al + 4% V) with a known concentration of hydrogen. In the reversible reaction $Ti + H_2 = TiH_2$, the equilibrium pressure is less than 10^{-13} atmospheres at room temperature, and 150 atmospheres at 900°C. Reaction is rapid at 300°C. This gettering reaction with hot titanium is in common use in geochemistry for separating hydrogen from oxygen and nitrogen (which react irreversibly) and from noble gases. Massive hydrides are prepared industrially by the same direct reaction process for hydrogen-based energy storage and nuclear applications.

Batches of a few grams of titanium alloy specimens have been doped with hydrogen using a simple closed gas handling system. Means are provided for pumping away air and hydrogen from samples at high temperature and for admitting a known pressure of hydrogen in a calibrated volume at room temperature, then raising the temperature of the system to carry out the reac-

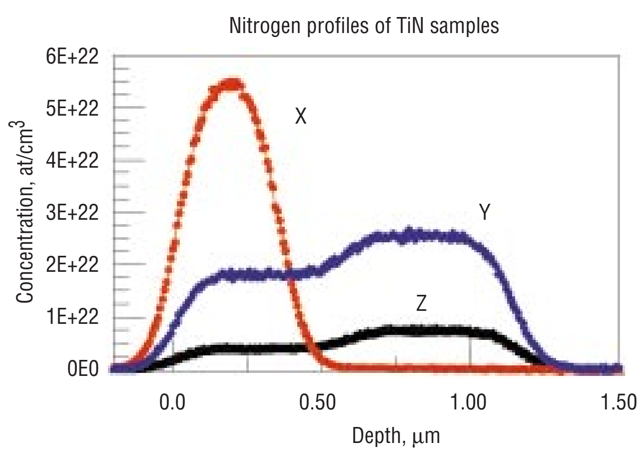

FIGURE 1. Three titanium samples from a previous study indicating nitrogen non-uniformity and less than one-to-one stoichiometry.

G. P. Lamaze, R. M. Lindstrom,
R. L. Paul, and R. Zeisler
Analytical Chemistry Division
National Institute of Standards and Technology
Gaithersburg, MD 20899

tion. The accuracy of the doping is limited by that of the pressure measurement, better than 0.5%. The amount of H in the metal samples was measured in 100-mg specimens by cold-neutron prompt-gamma activation analysis. The quantity measured by this technique and by gravimetry agreed with the volume of gas added. Eighty-gram cylinders of Ti alloy have been loaded by the same procedure, and the uniformity of doping verified elsewhere by quantitative neutron tomography.

These measurements indicate that Standard Reference Materials of hydrogen in titanium alloy can be made and certified by quantitative preparation and analysis as two independent methods, as is done with chemical solution standards at NIST. An apparatus has been constructed to dope 1-kg quantities of metal for Standard Reference Materials.

Titanium nitride films. Reference materials are a critical part of semiconductor metrology since they establish a means of comparison of data taken by different methods or between model and experiment. SEMATECH has requested a titanium nitride Standard Reference Material as one of their highest needs. A prototype SRM has been made by ion beam sputtering onto 75-mm diameter silicon wafers that were then cut into 10-mm squares. The thickness of the TiN was about 100 nm. Four squares plus a blank were analyzed by NDP to determine the total nitrogen concentration. The concentration was determined relative to a boron concentration standard. The relative count rates of the nitrogen and boron samples were adjusted by the ratio of the nitrogen to boron cross sections (1.819/3840). Statistical uncertainties are about 1% (1 σ) and the overall normalization uncertainty is 2% (1 σ) due to the uncertainty of the nitrogen section. An approximate 3% fall-off of the nitrogen concentration from center to edge of the original wafer was observed. A measure of the titanium concentration on each square was made by the technique of activation analysis. This allows a determination of the stoichiometry of the TiN.

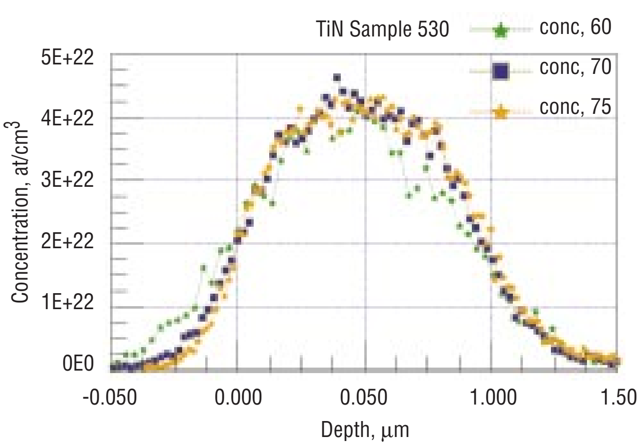

FIGURE 2. Proposed SRM material with expected stoichiometry. Measurements taken at different angles indicate same nitrogen distribution with differing resolution functions.