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IN ICF TARGETS**

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ABSTRACT

Capsules that contain doped GDP layers must be characterized for dopant concentration level and uniformity. X-ray μ -fluorescence (XRF), with its unique capability to quantitatively determine concentrations of most elements simultaneously and non-destructively, and in an efficient manner, is generally the method of choice for total dopant ($Z > 11$) concentration within ICF capsules. Dopant homogeneity (as well as concentration) within the target has been determined using Rutherford Backscatter Spectroscopy (RBS). Other methods which have provided information are SEM/EDXS; combustion analyses; mass spectroscopy and thermogravimetric analysis (TGA)

I. INTRODUCTION

The Inertial Confinement Fusion (ICF) program is investigating the conditions necessary to achieve in a laboratory environment, short-lived, miniature explosions which will release energy by thermonuclear fusion. In the laboratory, hollow, multi-layered spheres are used to contain the thermonuclear fuel. Ablation of the sphere walls, using high-powered lasers or particle beams, results in compression and heating of the fuel to attainment of the conditions of extreme temperature and density necessary for fusion to occur.

Chemical dopants are generally added to the outer ablation layers, to the inner shells or mandrels, or as a gas in the interior void of ICF targets to act as spectroscopic temperature and/or density indicators in specific parts of the target. In addition, these dopants aid the experimentalists in diagnosing the implosion uniformity, temperature and mixing of the various target components during the different stages of the implosion. However, in order for this chemical doping to be of much help as a diagnostic, the doping level (total concentration) as well as

the distribution of the dopant within the target (homogeneity) must be known. There are a number of methods for diagnosing elemental concentrations and uniformity in materials. Unfortunately, not many of them fulfill the specific requirements needed to be of much use for the typical ICF target, which is usually a small hollow sphere (≤ 1 mm diameter), light (10's of μg), fragile and composed of several layers of differing composition.

The purpose of this paper is to detail the diagnostic methods utilized in the ICF target program to determine both the total concentration and homogeneity of chemical elements utilized as dopants in the ICF program.

II. METHODS OF ANALYSES

The ideal analysis method would be able to analyze a single ICF target capsule non-destructively. This ideal method would also be fast, accurate, sensitive, and have the ability to measure all of the elements in the periodic table, both for total concentration and homogeneity simultaneously. Unfortunately, no single method fulfills all of these constraints. However, since all elements can be induced to emit characteristic x-rays, and all elements will scatter particle beams, two methods are widely useful: x-ray Fluorescence (XRF) and ion beam spectroscopy, which includes both Rutherford Backscatter Spectroscopy (RBS) and Nuclear Resonance Analysis (NRA). In addition, the following techniques also occasionally provide useful information: Scanning Electron Microscopy/Energy Dispersive x-ray Diffraction (SEM/EDXS); Auger Electron Spectroscopy (AES) with ion milling; Mass Spectroscopy (MS); Thermogravimetric Analysis (TGA); and Atomic Absorption (AA). A discussion of the capabilities and limitations of each of these techniques (and others) is given in Ref. [1] as well as in numerous other publications. The two methods of greatest utility to the ICF program (XRF and ion beam

spectroscopy) are discussed briefly below.

In XRF analysis, an x-ray source is used to irradiate the specimen thereby causing the elements in the specimen to emit (or fluoresce) their characteristic x-rays. In an energy-dispersive x-ray system, such as the one utilized here, a detector system is used to measure the photon energies of the fluorescent x-rays for identification of the elements present, and to measure the intensities of the peaks for quantitative determination of the composition. In general all elements but low-Z elements (H, He and Li) can be routinely analyzed by XRF. However, the commercially available XRF system best suited to measure ICF capsules can only measure elements with $Z \geq 11$ (Na). Table I lists the capabilities of XRF with respect to analysis of ICF capsules.

RBS is used to measure both the homogeneity and concentration of elements (dopants) within a sample. RBS analysis is performed by bombarding a sample with a monoenergetic beam of high-energy particles, typically helium, with an energy of a few MeV. A fraction of the incident atoms scatter backwards from the heavier atoms in the near surface region of the target and are detected with a solid state detector that measures their recoil energy. The energy of the back-scattered particle is related to the depth and mass of the target atom, while the number of back-scattered particles detected is proportional to the concentration. This relationship is used to generate a quantitative depth profile of the upper few microns of the sample. Table II lists the capabilities of RBS with respect to analysis of ICF capsules.

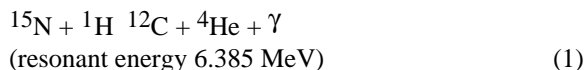
Table I
XRF Capabilities with Respect to Analysis of ICF Targets

Ability	Explanation
Non-destructive and fast	Allows measurements on actual targets in generally <5 minutes per target
Detects most elements in Periodic Table ($z > 11$)	Detects all element simultaneously – allows for ready detection of contaminants
Accurate	<10% error on actual target capsules for most elements
Sensitive	<0.1 atomic % for most elements on a single ~500 μm diameter capsule with a 5 μm wall
Efficient	Automated for improved through-put
Single calibration covers a wide range of target parameters	Development of precise analytical model allows for robust performance
Instrumentation commercially available at moderate cost (<200 K)	Allows for use in a production and/or research environment

Table II
RBS Capabilities with Respect to Analysis of ICF Targets

Ability	Explanation
Semi-destructive	$\sim 10^{13}$ atoms implanted; radiation damage possible in some polymers
Range of elements detected	Lithium to uranium
Accurate	No standards required; 5%–20%
Sensitive	1–10 at.% for low-Z; 0–100 ppm for high-Z
Lateral resolution	<5 μm to >1 mm
Depth resolution	2–30nm with a max. depth of ~20 μm with H^+
Instrumentation is generally large and relatively expensive	2 m x 7 m; \$500,000–\$1,000,000

Another specialized ion beam technique, NRA, has been utilized to determine the distribution of hydrogen (^1H) and deuterium (^2D) in a D doped glow discharge polymer (GDP), a common material in ICF capsules. In the NRA method, a beam of ^{15}N atoms is impelled into the target. The ^{15}N undergoes a nuclear reaction with ^1H present in the sample to generate carbon and helium plus a gamma ray:



This reaction is very sensitive (and specific) for hydrogen (~ 100 ppm atomic) and has a depth resolution of $\sim 3.3 \mu\text{m}$ in $(\text{CH})_x$ materials.

III. XRF METHOD

In quantitative analyses via the XRF method, the observed fluorescent x-ray intensities must be corrected for various factors: spectral intensity distribution of the incident x-rays; fluorescent yields; matrix enhancements and absorptions; geometry; detector efficiency; etc. Obviously, for the highest accuracy, calibration of the XRF instrument requires the use of appropriate standards. Since neither suitable commercial standards, nor software for analyzing samples of our particular geometry, are available for our rather unique application (mainly analyses of multiply layered hollow spheres) we have developed our own appropriate standards and models for precise instrument calibration.

The calibration of the XRF unit is essentially a three step process:

1. Determine the instrument sensitivity for the analyte of interest
2. Prepare and characterize samples of the appropriate geometry doped with the analyte of interest
3. Model results from step 2 to support the calibration and to allow for changes in sample parameters without the need for recalibration

Determining the instrument sensitivity, *i.e.* the number of analyte x-ray counts detected per atom per second in the absence of any appreciable absorption or enhancement effects, is accomplished first and takes care of effects due to detector efficiency as a function of fluorescence energy. Since chlorine (Cl) was the first element to be calibrated, this was accomplished by analyzing small, thin walled, Cl containing polystyrene spheres precisely measured for o.d. and wall thickness ($\sim 450 \mu\text{m}$ o.d. \times $\sim 3 \mu\text{m}$ wall). These hollow spheres were also analyzed by the commercial combustion method and thus contained an

accurately known amount of Cl. Instrument sensitivity for future dopants are then determined by referencing the analyte signal against the Cl in a thin film of sample containing a known stoichiometric ratio of analyte to Cl. For instance, in the determination of the instrument sensitivity for titanium (Ti), pure titanocene dichloride ($(\text{C}_5\text{H}_5)_2\text{TiCl}_2$) was dissolved in a benzene/polystyrene solution and cast as a thin film ($\sim 1 \mu\text{m}$ thick). Measurement of this film by the XRF system yields the sensitivity of Ti relative to Cl since the Ti:Cl ratio in the film is precisely 1:2. Using sensitivity values determined in this fashion allows for approximate calibration of the XRF system until the time consuming improved calibration process outlined below can be completed.

In calibrating the method for improved analysis of capsules the second step is to prepare capsules with varying thickness of GDP doped with a constant concentration of the desired analyte. Constant concentration of analyte is verified by performing the GDP coating process in steps. In the first coating step, mandrels are coated with a couple of microns of doped GDP and then analyzed. These capsules are then returned to the coater along with new uncoated mandrels. A second coating of a couple of microns is applied and analyzed. Analysis of the newly added shells confirms that the concentration of dopant in the second coating process was \sim identical to that in the first step. This process is continued until the final coating thickness is reached – usually about $40 \mu\text{m}$. After the coating steps are completed and the precise shell dimensions (o.d., total wall and layer thicknesses, mass and density) and XRF readings are taken, the shells are sent to a commercial elemental analysis laboratory for very precise determination of the total elemental concentrations (C,H,O,N and analyte of interest). A plot of the XRF signal (corrected for diameter) against doped GDP thickness (Fig. 1), in combination with the elemental analysis results by combustion, gives you an accurate calibration of the system for capsules of that particular size and analyte concentration.

The third step is modeling of the results with a model which includes explicit parameters for the pertinent physics and target dimensions. This modeling accurately allows for non-linear changes in various target dimensions and layers given the calibration constant determined by relating the calculated fluorescent intensities to the experimental observations from the previous step. Figure 2 illustrates conceptually all of the physical parameters taken into account by the theoretical model developed specifically for the ICF program.

Fundamental parameter methods for quantitative x-ray analysis requires, among other things, a knowledge of the spectral distributions of x-ray tubes used for sample excitation. The algorithm used in this model, developed by Pella, Feng and Small,² is based upon extensive

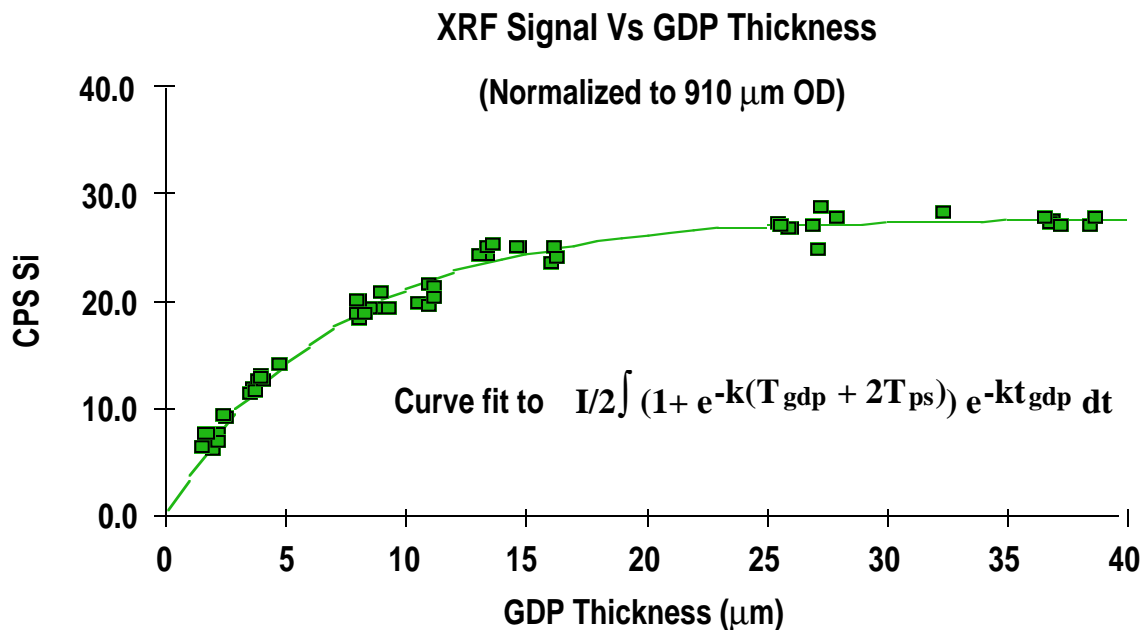


Fig. 1. Exponential curve fit of Si doped GDP data for a single Si concentration allows for an accurate calibration of the XRF system for capsules of this particular composition and analyte concentration.

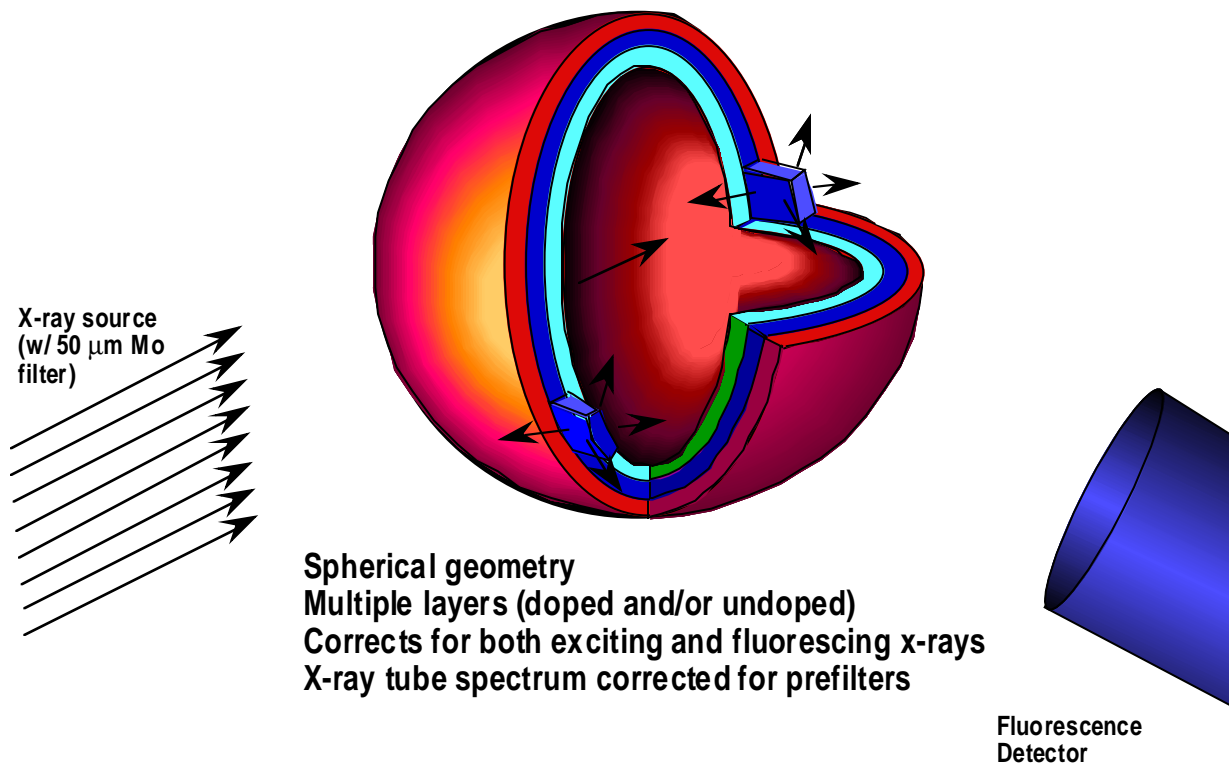


Fig. 2. The theoretical model includes explicit corrections for geometry, allows for multiple layers (doped and undoped), corrects for absorption of excitation and fluorescence x-rays, and x-ray filtering of the tube spectrum.

microprobe data and includes the calculation of the continuum and the ratio of the characteristic line(s) to the underlying continuum intensity at the wavelength of the characteristic lines. The equation for the x-ray tube continuum distribution expressed in terms of unit solid angle is:

$$I(\lambda) = CZ(\lambda/\lambda_0 - 1)(1/\lambda^2) f(\lambda) W_{ab}(\lambda) \quad (2)$$

where $I(\lambda)$ is in units of photons $\text{\AA}^{-1}(\text{e}^-)^{-1}\text{STR}^{-1}$ at wavelength λ ; $C = 2.72 \times 10^{-6}$ photons $\text{\AA}^{-1}(\text{e}^-)^{-1}\text{STR}^{-1}$; Z is the atomic number of the x-ray tube target material; λ_0 is the shortest wavelength allowed (corresponding to 40 keV here); $f(\lambda)$ is a term which corrects for absorption of continuum x-rays by the target; and $W_{ab}(\lambda)$ is a correction term for absorption by the Be window of the x-ray tube.

The ratio of the intensity of the characteristic/continuum x-rays is extracted from a graph of the characteristic/continuum ratios for various target elements with tube energies up to 50 keV.² We generally only use a Mo x-ray tube operated at a single voltage (40 keV).

Once the spectral distribution (corrected for source filters if utilized) impinging on the target is known, the next corrections required relate to the ICF capsule. Corrections for x-ray absorption of both the exciting x-rays and the fluorescent x-rays are calculated. This task is accomplished by subdividing the doped spherical capsule into its component layers. The doped layer is then further divided into $10^\circ \times 10^\circ$ segments (polar coordinates) which results in 648 (36×18) separate volume elements per doped layer (both the number of layers and the segment size are user selectable). x-ray absorption correction factors are calculated for each volume element, taking into account each volume element's location within the sample with respect to the x-ray source and detector. These correction factors are calculated on a SUN computer workstation, for both the exciting and fluorescent x-rays, utilizing elemental mass absorption coefficients for various capsule components. Elemental mass absorption coefficients as a function of x-ray energy are taken from data tables generated by Lawrence Livermore National Laboratories.³ The calculated intensity of the resulting fluorescence spectrum for each target is plotted as a function of doped layer thickness and compared to the experimental data (Fig. 3). A prefactor (which essentially relates to the instrument sensitivity factor) in the model data is then adjusted to give the best fit of the model data to the experimental data. Once this step is complete, recalibration of the XRF system for changes in target dimensions and elemental concentrations is readily accomplished by use of the model only. Figure 3 illustrates the expected intensity curves for various concentrations of silicon (Si) dopant and three different undoped inner mandrel thicknesses.

Development of this precise model allowed for the detection of a previously unnoticed small change in silicon concentration in one of our silicon (Si) doped GDP coating experiments. This small change in concentration is apparent when examining the fit of the model data to the experimental data shown previously in Fig. 3. If the model data is recalculated assuming a 7% decrease in Si concentration after the initial 14 μm 's of doped GDP had been deposited, the fit to the data is much better (Fig. 4). Analysis of the control samples put into the GDP coater at various times during the coating run are consistent with this observation of decreased Si doping level.

IV. ION BEAM METHOD

Results obtained by RBS are generally insensitive to sample matrix and typically do not require the use of standards. The energy of a back-scattered particle detected depends upon two processes: the loss of energy by the incoming particle due to the transfer of momentum to the target atom during the back-scattering event, and the loss of energy by the particle during transmission through the sample matrix (both before and after scattering). For scattering at the sample surface the only energy loss is due to momentum transfer to the target atom. As the beam penetrates farther into the sample, energy is lost in glancing collisions with the nuclei of the target atoms as well as in interactions with electrons. For a 2 MeV He atom, the energy loss is in the range of 100 eV/nm for organic polymers and is reasonably linear down to 0.5 MeV. These facts allow us to use RBS to determine the thickness of layers and in elemental depth profiling. The ratio of the projectiles energy after a collision to its energy before collision (E_1/E_0) is defined as the kinematic factor K :

$$K = \left\{ \frac{\sqrt{1 - \left[\left(\frac{m_1}{m_2} \right) \sin \varnothing \right]^2} + \left(\frac{m_1}{m_2} \right) \cos \varnothing}{1 + \left(\frac{m_1}{m_2} \right)} \right\}^2 \quad (3)$$

where M_1 is the mass of the incident particle; M_2 is the mass of the target atom; and \varnothing is defined as the angle between the trajectory of the particle before and after scattering.

The relative number of particles back-scattered from a target atom is related to the differential scattering cross section of the atoms. A rule of thumb is that the scattering cross section is basically proportional to the square of the atomic number Z of the target species. This means that RBS is much more sensitive for detection of heavy elements than light elements, such as B or C. However, because there is a much larger separation in energies of particles back-scattered from light elements than from heavy elements, the mass resolution for light elements is

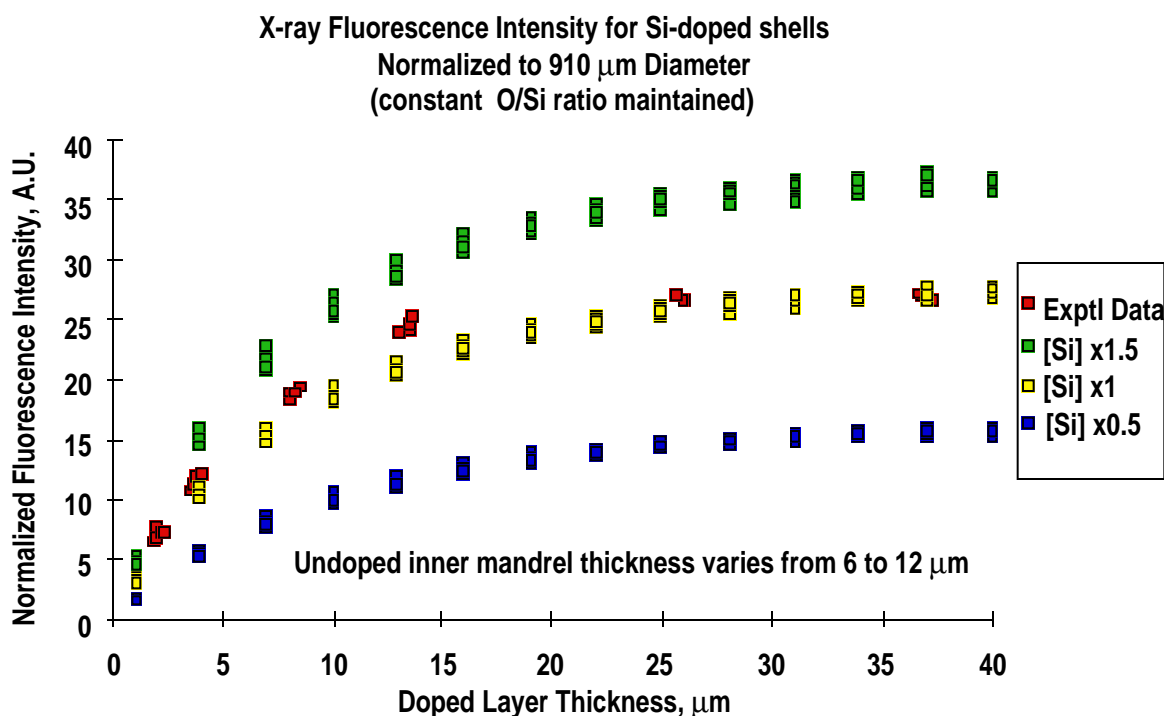


Fig. 3. The calculated intensity of the resulting fluorescence spectrum for targets with an undoped inner mandrel thickness of 6, 9 or 12 μm and three different Si concentrations is plotted as a function of doped layer thickness. The middle curve ([Si] \times 1) is the fit of the experimental data.

much better than for heavy elements. Thus, you could detect much lower concentrations of elements like tungsten, but you could not distinguish it readily from an element like rhenium. On the other-hand, the detection limit for light elements like C is not as good, but you could readily distinguish C from O.

The RBS spectra of 3 Si doped GDP films, analyzed with a 2.0 MeV He beam, shown (overlaid) in Fig. 5 illustrate this principle and the capabilities of this method.

The first spectrum shown in Fig. 5 is that of unpyrolyzed, Si doped GDP. The leading high energy peak is flat and at \sim 1.25 MeV which shows that the Si is doped uniformly throughout the GDP layer. The intensity of the peak determines the concentration of the Si in this layer (\sim 6 at.%). The onset of the oxygen peak reveals that it too is present uniformly throughout the layer and is present at \sim 8 at.%. The second spectrum shown is the same GDP sample after heating to 300 $^{\circ}\text{C}$. The spectrum is identical to that of the first which shows that the sample suffered no adverse effects upon heating, such as loss or migration of silicon. The third spectrum is that of a Si doped GDP layer which has about a 3 μm thick undoped GDP on top. The very small shoulder on the leading edge of the spectrum shows that Si did not migrate out into the undoped layer during the layering process. Had the Si migrated, the onset of the Si peak would have been at

considerably higher energy. Clearly, in the quest to provide elemental homogeneity and concentration information to the target experimentalists, RBS provides a great deal of information.

V. OTHER METHODS

Other methods are utilized from time to time to provide information on dopant concentration and stability of the doped polymer. However, since these methods are not used on a regular basis a detailed discussion of these methods is not presented. Instead, a list of the methods utilized and the relevant information provided in support of the ICF program is presented in Table III.

VI. CONCLUSIONS

XRF and RBS are the two primary methods utilized in the ICF program for determining dopant concentration and dopant uniformity in capsules prior to being utilized as targets. The ability of XRF (with modeling) to provide fast and accurate elemental identification and concentration information in a nondestructive fashion, and at a reasonable cost, makes it the preferred choice. Since XRF does not provide the needed chemical homogeneity information, a second method – RBS, is frequently

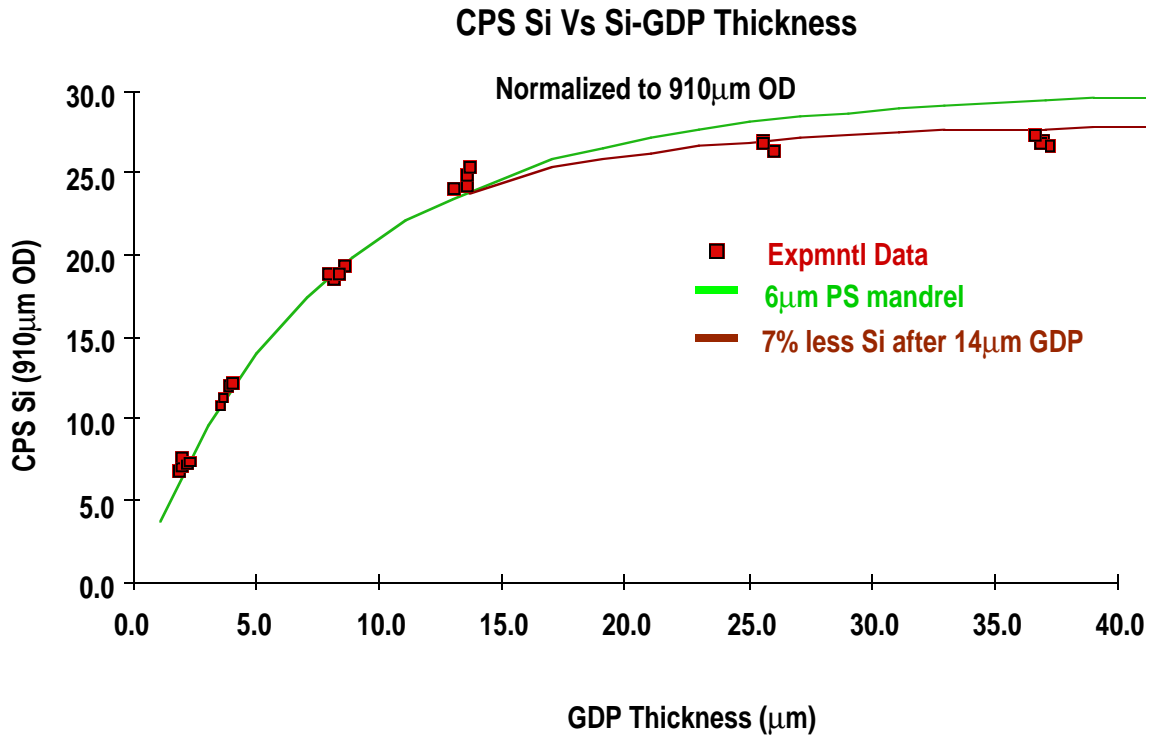


Fig. 4. The model data is recalculated assuming a 7% decrease in Si concentration after the initial 14 μm of doped GDP had been deposited. The fit to the experimental data is improved significantly.

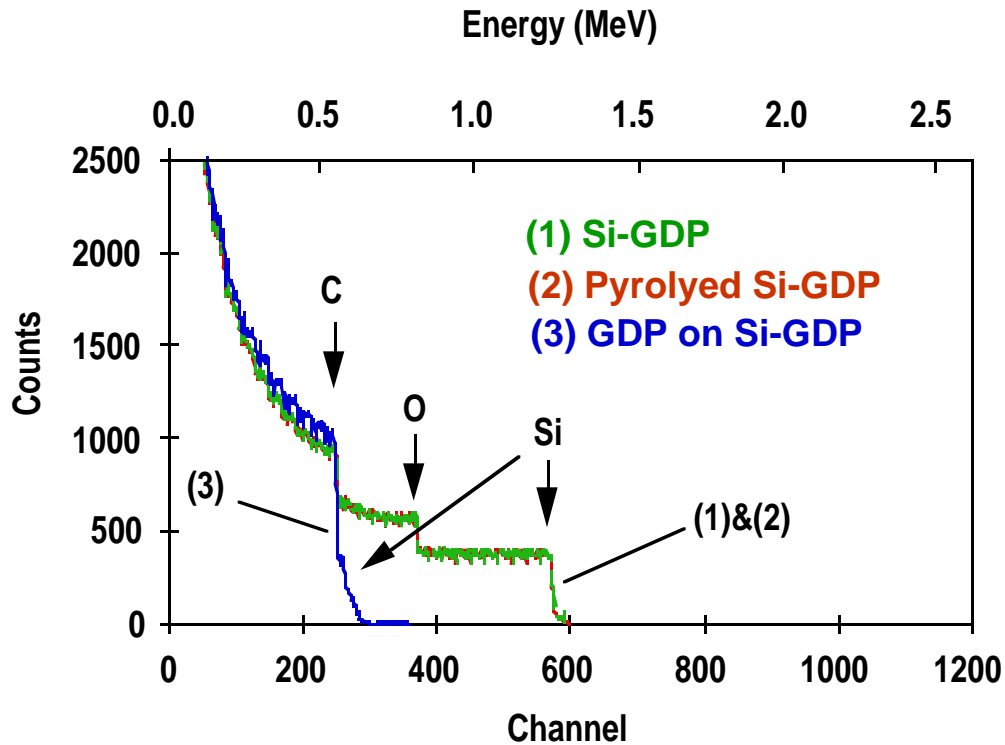


Fig. 5. Three RBS spectra of Si doped GDP samples are shown – (1) Pure Si-GDP; (2) Sample #1 after pyrolysis; (3) ~8 μm normal GDP on top of Si-GDP. Spectra indicate that the Si is stable during pyrolysis and during overcoating.

Table III
Other Dopant Analysis Methods

Method	Information Obtained
NRA	Concentration and homogeneity of H impurities in D doped GDP
AES with ion milling	Homogeneity of Ti in polystyrene
SEM/EDXS	Homogeneity (to ~2 μm depth) of dopants in the lateral (x-y) direction; cross-sectional analysis provides depth profiling
High Resolution Mass Spectroscopy	Overall levels of H contamination in D-doped GDP
Combustion technique	High accuracy determination (~1%) of total concentration of the elements in a sample (destructive). Used for calibration of XRF.
TGA	Determines thermal stability of doped GDP polymers

utilized. However, the RBS method is more time consuming than XRF and requires specialized and expensive instrumentation which prevents its use as a day-to-day production tool. When specific information not obtainable by XRF or RBS is required, or confirmation of information is needed, other analysis techniques are employed.

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REFERENCES

1. C. Brundle, C. Evans, and S. Wilson, *Encyclopedia of Materials Characterization*, Butterworth-Heinemann and Manning (1992).
2. P. Pella, L. Feng, and J. Small, "An Analytical Algorithm for Calculation of Spectral Distributions of X-ray Tubes for Quantitative X-ray Fluorescence Analysis," *X-ray Spectrometry*, **14(3)**, 125 (1985).
3. "Compilations of X-ray Cross Sections," Lawrence Livermore National Labs document number UCRL-50174-SEC 2-R1 (1969).