Low Energy XRF (LE-XRF) in Semiconductor Metrologs

Application Note

By Michael Lun, Benjamin Stripe, Frances Su, Shane Pauker, Wenbing Yun, Sylvia Lewis

Abstract

Micro x-ray fluorescence (μXRF) has emerged as an invaluable analytical technique in the semiconductor industry, offering non-destructive elemental analysis with high sensitivity for dopants and thin film thicknesses. μXRF is conventionally performed at high x-ray energies (>5 keV) and is considered a high atomic number (high Z) metrology system. However, what is often overlooked is that μXRF becomes even more powerful at lower x-ray energies. This applications note explores the capabilities of AttoMap at low energies for critical applications in semiconductor metrology.

Overview of AttoMap-310™

Micro X-ray fluorescence (μXRF) spectroscopy has emerged as a valuable analytical technique in the semiconductor industry, offering a means of non-destructive elemental analysis with high sensitivity of dopants and thin films. μXRF is conventionally performed at high x-ray energies (5 keV or above) and is considered a high atomic number (high Z) metrology system for dopant concentration and thin film thicknesses for quality control, process optimization, and failure analysis in semiconductor fabrication.

Performing μXRF at low x-ray energies provides **powerful benefits** over conventional high-energy μXRF, including orders-of-magnitude higher sensitivity to low-Z elements and greatly improved sensitivity and acquisition times for the lower energy (L and M lines) of high-Z elements. This is due to x-ray optics' collection efficiency increasing as the ***square*** of wavelength. Despite its numerous advantages, the major bottleneck of low-energy μXRF is the low brightness of x-ray sources that produce low-energy x-rays, as well as the significant challenges in manufacturing low-energy x-ray optics.

After extensive developments, Sigray has developed the AttoMap-310, which delivers **breakthrough performance for low-energy μXRF**. The AttoMap-310 features Sigray's patented high-flux x-ray source design, utilizing actively cooled diamond to achieve high power loading, along with high-efficiency, axially symmetric x-ray optics.

The system has been adopted rapidly by the semiconductor industry [1] for a wide range of elemental monitoring applications, including:

- **Aluminum**, for work function tuning in transistors
- **Fluorine**, a residue from processing (e.g., etching)
- **Germanium**, used in SiGe structures for gate-all-around and used as a metrology endpoint for etching
- **Molybdenum Nitride**, commonly used as a thin film in gate electrodes and in memory applications

Additional applications successfully performed by AttoMap include Boron, Titanium Nitride, Oxygen, and Zirconium

Figure 1: Sigray's AttoMap

AttoMap-310™ Micro X-ray Fluorescence (μXRF) Microscope

Sigray's AttoMap-310 μXRF provides rapid analysis of both low atomic number (low-Z) elements down to boron (B) and the low-energy fluorescence lines (e.g., L and M-Lines) of high atomic number elements. Its unparalleled performance is enabled by several major innovations in critical x-ray components, including:

1. **Patented X-ray Source w/ Multiple Targets:** Sigray's x-ray source allows users to select up to five different x-ray target materials to tune incident x-ray energy, maximizing sensitivity by up to two to three orders of magnitude. These targets include Sigray's patented **ceramic x-ray source targets**, which provide substantially higher power loading and brightnesses compared to conventional x-ray target materials such as Aluminum. Particularly advantageous for semiconductor applications are Sigray's SiC x-ray targets, which produce an ultra-bright Si line that avoids exciting Si fluorescence from the substrate/wafer, and a Calcium-based target for high-efficiency Sn/Ag ratio measurements. Other available targets include Au, Cr, Cu, etc.
2. **Proprietary X-ray Optics:** Unlike conventional μXRF systems that use polycapillary optics, the AttoMap-310 employs Sigray's proprietary axially symmetric x-ray optics. These optics provide superior performance at low x-ray energies and can be configured to deliver over 99% of a high-flux beam

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within a 40µm test pad (or focus to a small 3–5 µm achromatic x-ray spot). Additionally, Sigray's optics enable the detector to be positioned much closer to the sample than polycapillaries optics, resulting in significantly greater fluorescence collection.

3. **Goniometer Stage (θ-2θ):** The AttoMap-310's sample stage and SDD can rotate to achieve near-grazing incidence angles on samples, maximizing the sensitivity of low-energy x-rays. Rotation angles can also be adjusted to eliminate diffraction peaks present in Si wafers.
4. **Vacuum Enclosure:** The AttoMap-310 operates within a vacuum chamber that achieves <10E-5 torr, which was designed to enable ultra-low concentrations of carbon and oxygen upon request by semiconductor customers.

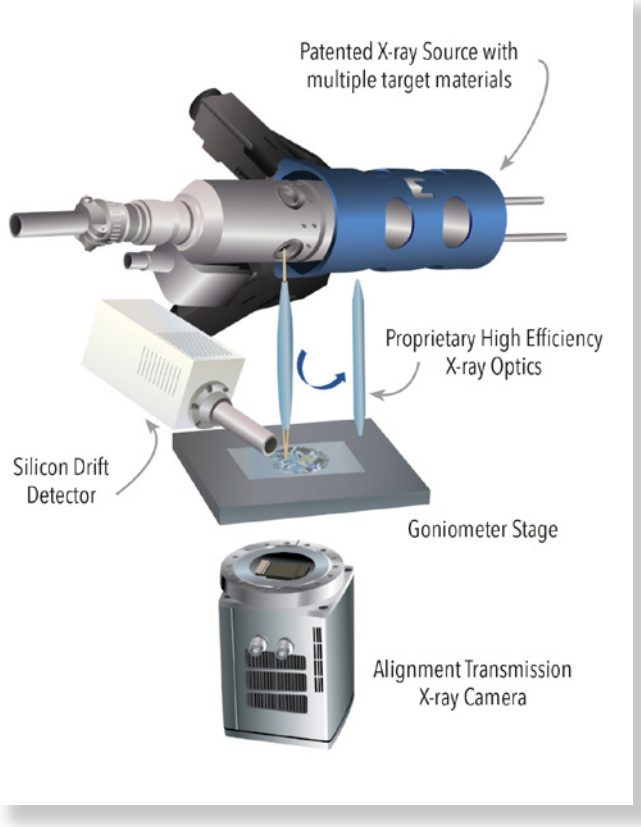

Figure 2: AttoMap interior schematic. The system uses a patented ultrahigh brightness x-ray source with multiple patented x-ray targets (including ceramic targets with superior performance in semiconductor applications), high efficiency x-ray optics, and a system design that includes a goniometer for optimal source-sample angles (to maximize sensitivity & remove diffraction peaks).

Experiments and Results

The AttoMap-310 was applied to challenging semiconductor samples (Al, F, Ge, Mo, N) to demonstrate the system's performance for a range of low energy µXRF. All scans used Sigray's patented SiC anode and proprietary axially symmetric x-ray mirror lenses.

I. Aluminum

Al is an important work function tuning material in modern and future transistors [2], resulting in requirements to be able to measure ~5Å Al with sub-Angstrom precision. However, existing LE-XRF approaches suffer from the reliance on Al-based x-ray sources (which cannot excite Al). Alternatively, higher x-ray energies can be used (e.g. Cr at 5.4 keV), but they have poor fluorescence cross-sections for Al and suffer from the presence of a high background from the Si wafer. This background not only contains Si fluorescence at 1.74 keV, but also has a long low energy "tail" due to inelastic scattering (e.g. Raman) that significantly weakens sensitivity to Al (1.486 keV) [3].

The AttoMap-310's patented silicon-based x-ray source target produces a nearly monochromatic x-ray beam at 1.74 keV, which is advantageous because it does not excite the Si bulk of the substrate (silicon's absorption edge is 1.84 keV). Moreover, this energy is **optimal** for maximizing Al fluorescence (the Al-Kα absorption edge is 1.56 keV). Indeed, the Si line provides >700X greater Al signal than conventional x-ray targets such as Mo-Kα.

In this experiment, a set of four samples, including a laddered sample of ultra-thin Al films and a reference blank sample, was provided by a leading semiconductor manufacturer. Although the equivalent Al thicknesses were not provided, they were sufficiently challenging to be of significant interest for next-generation devices. The customer had pre-determined the expected spectral trend.

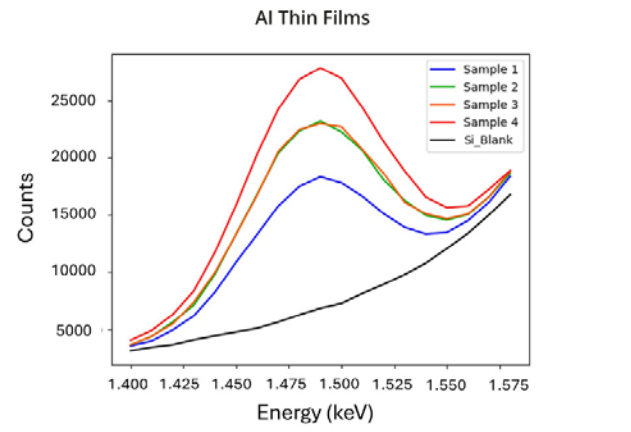

Figure 3: XRF scan of Al thin film samples at the Al peak (1.486 keV) demonstrating the expected spectral trend.

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Figure 3 shows results from a challenging set of laddered Al thicknesses. We can see well-defined Al peaks for each sample in accordance to the trends expected by the customer.

II. Fluorine

F is used in many semiconductor manufacturing processes for purposes such as etching, surface cleaning, and as a dopant. When used for etching or surface cleaning, it is especially important to ensure that no fluorine remains on the wafer, as it may cause detrimental effects, including defects, doping effects, corrosion, etc. [4-5].

The AttoMap demo lab was provided with a laddered sample containing trace levels of F (down to 0.3 At%) to scan using the AttoMap-310. Complementary measurements of Atomic % acquired by X-ray Photoelectron Spectroscopy (XPS) were provided as a reference. Results from the AttoMap scans are shown in Figs. 4. Fig. 4a shows the raw spectra of the F peak at 0.677 keV. A gaussian fit was applied to the F peak, and the fitted background was subtracted to determine the net F counts. Fig. 4b shows the plotted net counts, demonstrating a clear linear relationship (R^2=0.956).

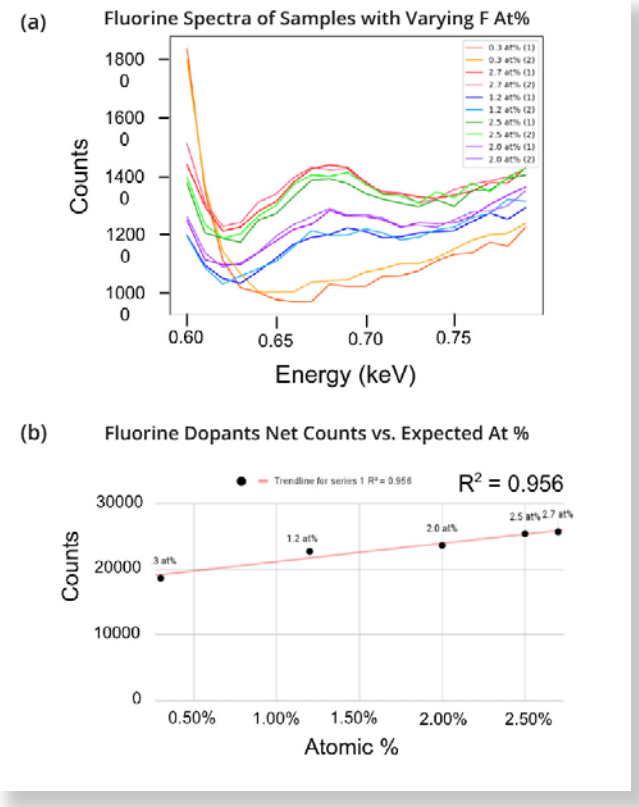

Figure 4. AttoMap results for a laddered sample of Fluorine (F) thin films on a silicon substrate. (a) Raw spectra around the F-Kα peak (0.677 keV) and (b) Net counts vs. XPS measurements of At %, showing good linearity.

III. Germanium

As a thin film, Ge has many applications, ranging from high-speed electronics (e.g., MOSFETs) to optoelectronics, MEMS and NEMS devices, and more. Ge has also recently become a major focus of metrology due to the increasing usage of SiGe/Si stacks for gate-all-around (GAA) devices [6]. In standard processes, SiGe is removed by etching to form a cavity for the gate's inner spacer. Because hard x-ray μXRF (e.g., >7 keV) is achievable using conventional x-ray components, equipment vendors have approached this challenging problem by measuring the Ge Kα line at 9.8 keV [6]. Although fluorescence *yield* (the percentage of x-rays absorbed that produce an XRF signal) is larger when using higher energy x-rays, the **overall fluorescence signal** for Ge is greater when using low-energy x-rays due to their significantly higher absorption (Fig. 5).

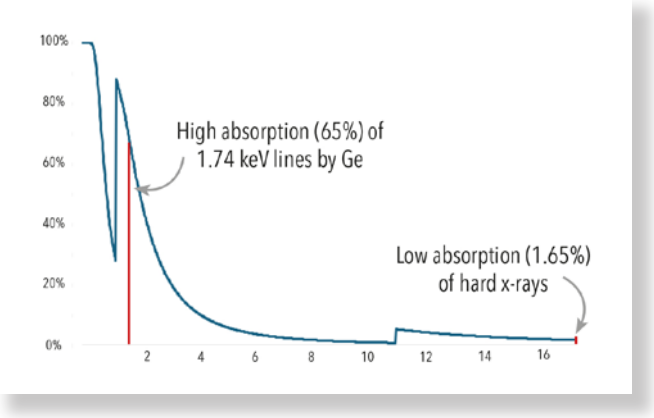

Figure 5. Percentage x-rays absorbed by 5nm of Ge as a function of x-ray energy. The majority (65%) of low energy Si x-rays (1.74 keV) are absorbed, while only 1.65% of hard x-rays produced by a Mo target (17.4 keV) are absorbed. Data from CXRO (henke.lbl.gov).

In addition to the increased fluorescence signal enabled by operating at low x-ray energies, Sigray's AttoMap also benefits from the significantly higher brightness of its silicon-based source compared to conventional x-ray sources, as well as the exponentially larger solid angle of its x-ray optics for low-energy x-rays. These factors provide well over a 100X gain in speed and sensitivity compared to conventional high-energy μXRF approaches.

For this measurement, samples of low-dosage Ge were prepared (Table 2) and scanned in the AttoMap-310, with the incident x-ray beam at both normal incidence and low incidence (10° to the sample surface, which provides >10X net counts compared to normal incidence). Both configurations successfully determined Ge dosages with high R^2 values (0.994 for both). The lowest limit of detection (LLD) for the low-incidence data is calculated to be 4.35E11 atoms/cm^2.

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Sample	Ge Dosage (atoms/cm^2)
1	0
2	3.0 x 10^{13}
3	7.1 x 10^{14}
4	1.5 x 10^{14}
5	3.5 x 10^{14}

Table 1. Dosages of the Ge thin film samples measured. Sample 1 is bare silicon provided as a reference.

Fig. 6 shows the normal incidence results, while Fig. 7 shows the low-incidence results. Net counts are produced using non-negative matrix factorization (NMF) spectral decomposition built into the AttoMap Analysis software. These net counts are plotted as trend lines to validate data linearity.

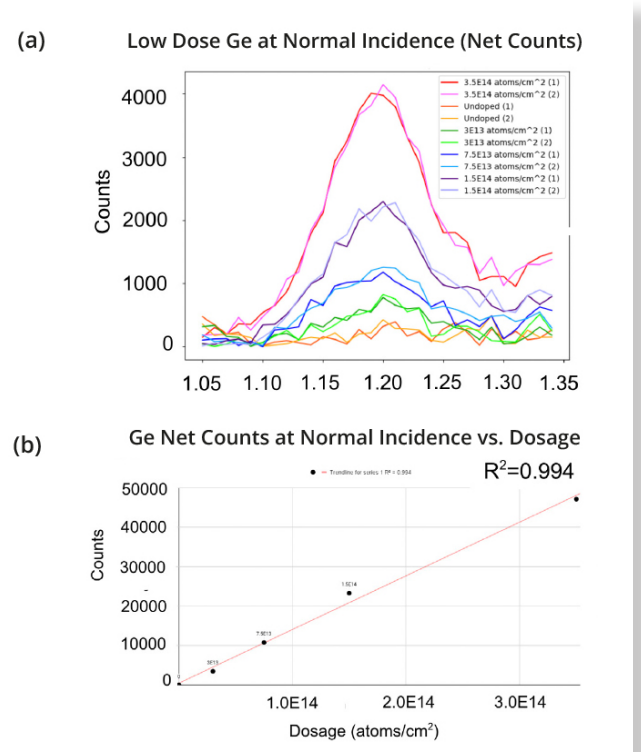

Figure 6. XRF of a laddered sample set of low concentration Ge acquired at normal incidence. (a) Derived Ge net counts after spectral decomposition using NMF and (b) Plot of XRF net counts as a function of dosages showing excellent linearity (R^2=0.994)

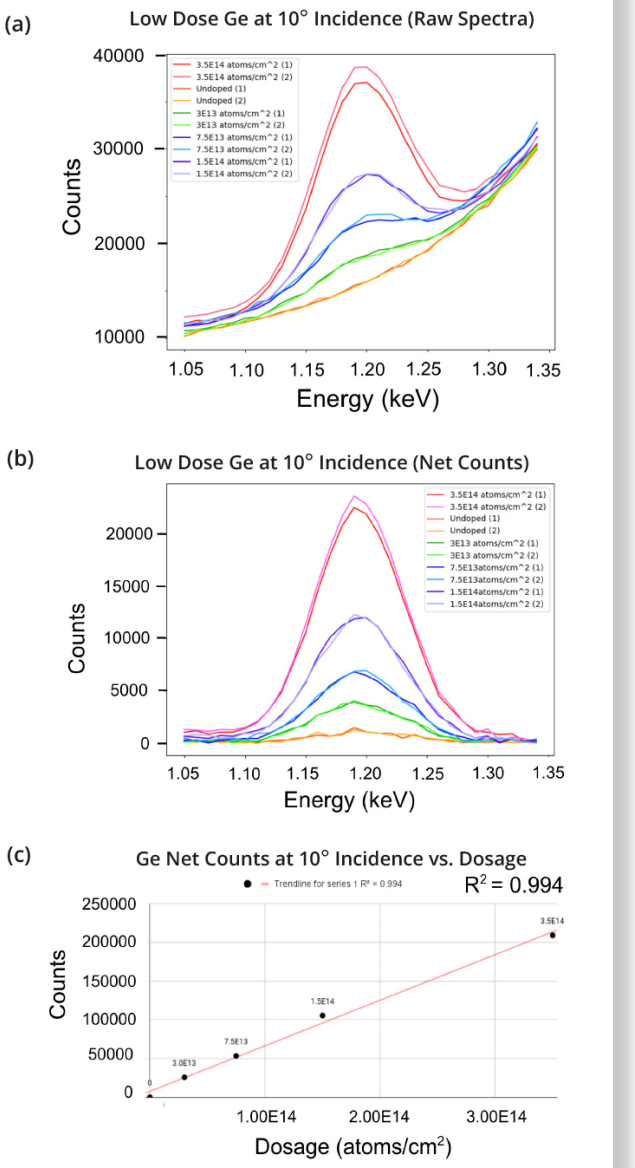

Figure 7. Scans of the laddered low dose Ge samples performed using a 10 degree incidence angle, showing better signal-to-noise (SNR) in the spectra over the normal incidence angle data of Fig. 6. (a) Raw spectra; (b) Net counts after spectral decomposition using NMF; and (c) Trend lines showing excellent linearity.

IV. Molybdenum Nitride:

Molybdenum nitride thin films play a diverse and important role in the semiconductor industry, including serving as a gate electrode in MOSFETs due to their high work function and compatibility with high-κ dielectrics [7]. As a thin film, molybdenum nitride also exhibits good adhesion to materials like silicon and can act as a diffusion barrier, preventing metal migration between layers due to diffusion.

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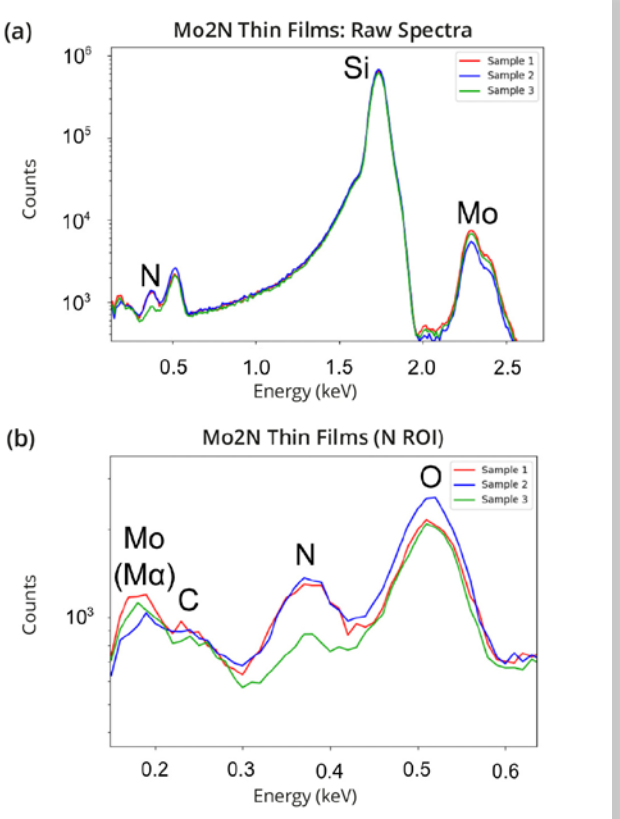
By modulating the atomic ratios of Mo and N, the properties of the molybdenum nitride films can be altered to optimize properties such as work function, resistivity, and thermal stability of the thin film.

In this experiment, three samples with varying amounts of Mo and N on Si (dosages provided in Table 3) were scanned in AttoMap. Results are shown in Fig. 8 (a-c). To maximize sensitivity, Mo Lα (2.292 keV) was monitored instead of its Kα (17.4 keV), achieving a **>57X sensitivity gain.** N Kα (0.392 keV) was also measured. Notably, the ultra-low energy Mo M-line emission (0.193 keV) is observed and follows the expected Mo trend. Fig. 8(a) presents the raw spectra, while Fig. 8(b) and 8(c) display zoom-ins of the N Kα and Mo Lα spectral lines, respectively.

Sample	N Dosage (E15 atoms/ cm²)	Mo Dosage (E15 atoms/ cm²)
1	24.3	30.8
2	26.7	19.7
3	10.2	27.9

Table 2. Customer-provided dosages of the molybdenum nitride thin film samples measured.



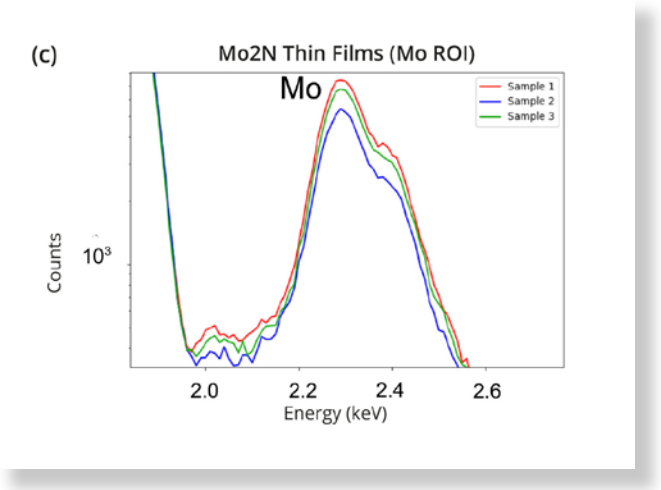


Figure 8. XRF scans of Mo2N films deposited on a Si substrate. (a) Raw XRF spectra showing both the N (0.392 keV) and Mo (2.292 keV) peaks; (b) Zoomed-in region around N which also includes Mo-Mα, C-Kα, and O-Kα peaks; (c) Zoomed-in region around the Mo-L lines.

Summary

Sigray's AttoMap-310 XRF microscope provides the semiconductor industry with the highest performance μXRF metrology tool for critical applications, such as residue measurements of Ge, dopant measurements of Al, and more. In this applications note, we have applied AttoMap to several samples containing low-dose elements used in today's semiconductor fabrication processes. This exceptional performance is made possible by a combination of Sigray's patented innovations, including its unique x-ray source using multiple targets (including SiC), proprietary high efficiency x-ray optics, unique scanning geometry using a θ-2θ goniometer, and high-vacuum enclosure.

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