Application note

Calibrating ablation rates for femtosecond-laser XPS depth profiling with the Hypulse Surface Analysis System

Introduction

X-ray photoelectron spectroscopy (XPS) depth profiling generates chemically specific information as a function of depth and is used across a wide range of applications, including the development of thin films and the analysis of coatings. A challenge of traditional XPS depth profiling is that ion sputtering can significantly alter the sample, leading to changes in oxidation state, elemental redistribution, or interface broadening. This can make it difficult to determine whether any changes seen with XPS are representative of the sample or simply artifacts of the measuring process, convoluting our understand of the true composition of the material. Such ambiguity can be particularly detrimental for processes such as failure analysis.

Femtosecond-laser ablation (fs-LA) utilizes a fundamentally different mechanism to remove material, and has recently been proposed as an alternative to ion-beam depth profiling. With fs-LA, energy is deposited on ultrafast timescales, limiting thermal diffusion and thus reducing chemical modification. This facilitates predictable material removal with the potential for fine depth control, as it is relatively easy to control the laser fluence at the sample surface. The Thermo Scientific™ Hypulse™ Surface Analysis System integrates fs-LA directly with XPS, helping to preserve chemical information and interfaces during depth profiling.

Calibrating laser ablation

Laser conditions can be calibrated to the amount of material removed; this can be vital for comparing the fs-LA depth profiling results from samples with the same composition. Operating just above the ablation threshold allows incremental, reproducible material removal without entering melt-dominated or plasma-driven ablation regimes. In the near-threshold regime, the depth of material (d) removed by a single femtosecond laser pulse follows an empirical logarithmic relationship, where F is the applied laser fluence, F_{th} is the single-pulse ablation threshold fluence, and S is a material-dependent slope parameter:

$$d=S\ \ln\left(\frac{F}{F_{th}}\right)$$

If the single-pulse ablation threshold fluence is known, this equation can be used to calculate the amount of material removed per laser exposure for any applied fluence. This application note describes how F_{th} can be determined though a simple process where data is collected at three different laser conditions for a sample with a known thickness.

Experimental procedure

The Hypulse System employs a femtosecond laser source with a 1,030 nm wavelength. Pulse energy is controlled through a motorized attenuator, enabling small, precise changes in the laser fluence at the sample. To create a depth profile, a static, single-pulse ablation approach is typically used, alternating laser ablation with XPS acquisition to create a composition profile.

The example specimen used in this application note consists of a $TaN_{1.5}$ film deposited onto a silicon wafer (composition verified by Rutherford backscattering spectrometry). A 435 nm film thickness was measured with SEM cross-sectioning on a Thermo Scientific™ Apreo ChemiSEM™ System (Figure 1).

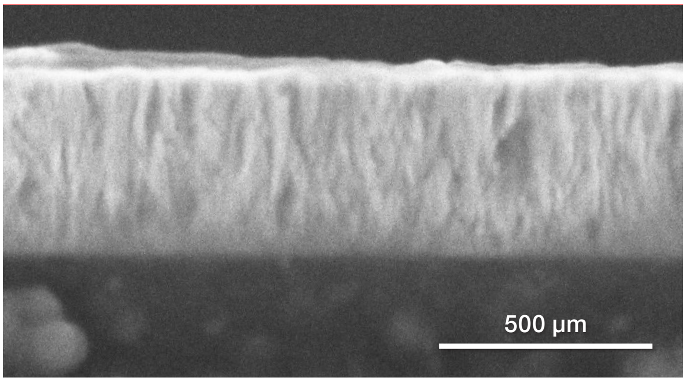


Figure 1: SEM fracture cross-section of the reactively sputtered TaNx thin film.

The remaining sample was loaded into the Hypulse System, and three depth profiles were collected at laser energies of 300, 400, and 500 µJ (Figure 2). These three profiles took 70 minutes to collect in total.

Once the profiles have been acquired, the interface position can be determined by finding the ablation level where the overlayer makes up 50% of the bulk film composition. Based on the ISO methodology for depth determination from a profile (ISO 17109:2022), this corresponds to the removal of 435 nm of material.

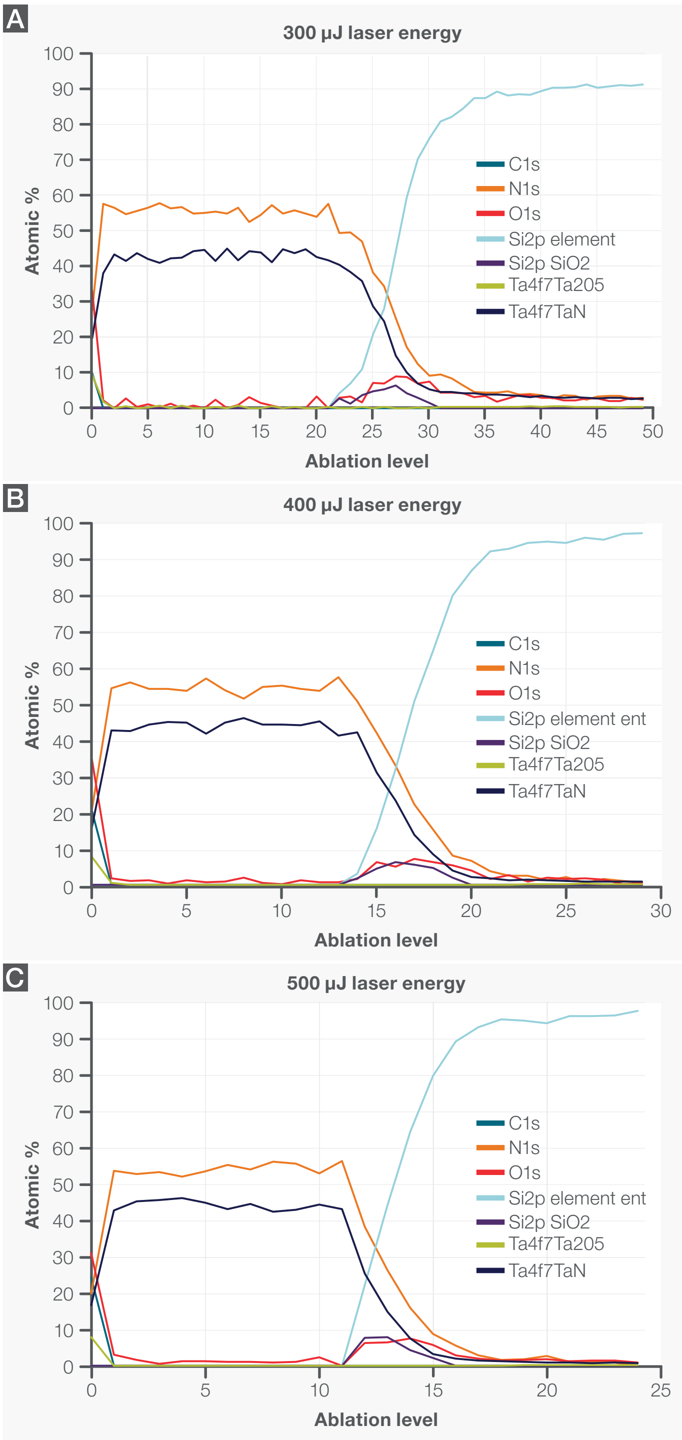


Figure 2: fs-LA profiles for the 435-nm-thick TaN film collected at (a) 300, (b) 400, and (c) 500 µJ laser energies. These are plotted as a function of ablation level, showing the compositional changes as a function of the number of ablation steps that have taken place.

The laser energy, together with the area illuminated by the laser and the beam intensity profile (which are measured during instrument set-up with a beam imaging module), can be used to calculate the laser fluence (*F*). The depth of material removed can be plotted against ln(*F*), and should result in a straight line; the gradient and intercept can then be used to calculate the ablation threshold (F_{th}). These values can subsequently be used to create a calibration plot; this allows for easy calculation of the laser energy needed to remove a desired amount of material per ablation step (Figure 3).

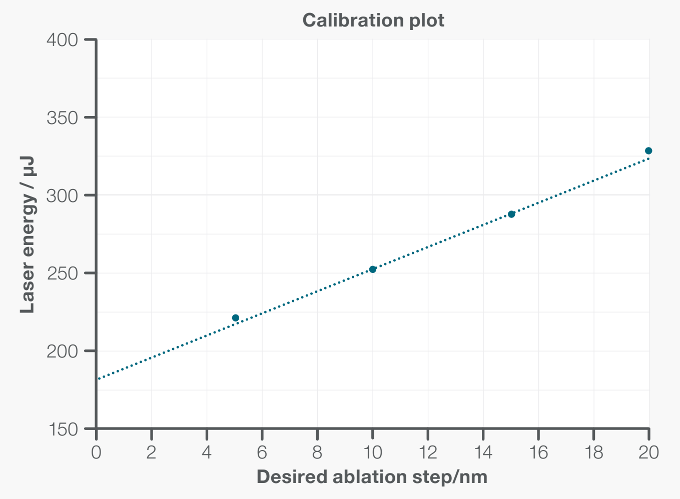
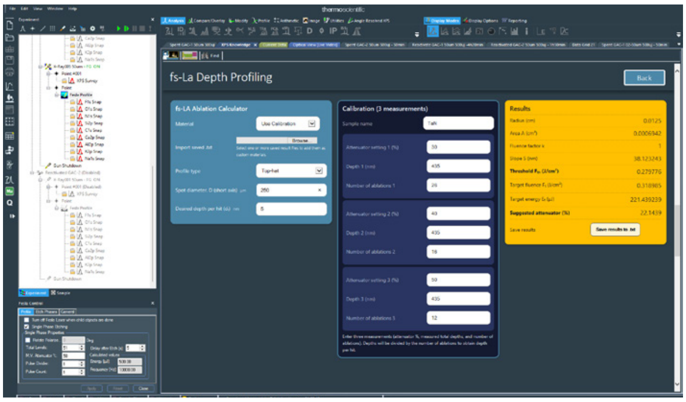


Figure 3: Calibration plot for the TaN film, showing the correlation between the energy of the laser and the depth of material that is removed.

Thermo Scientific Avantage Software is supplied with the Hypulse System and contains a calculator within the Knowledge View tool that further streamlines this analysis. Calibration data is simply entered into the tool and it automatically generates the required laser energy for a desired ablation rate (Figure 4).



fs-La Depth Profiling

fs-LA Ablation Calculator

Material: Use Calibration

Import saved .txt: Select one or more saved result files to add them as custom materials.

Profile type: Top-hat

Spot diameter, D (short axis) µm: 250

Desired depth per hit (d₀) nm: 5

Calibration (3 measurements)

Sample name: TaN

Attenuator setting 1 (%): 30

Depth 1 (nm): 435

Number of ablations 1: 26

Attenuator setting 2 (%): 40

Depth 2 (nm): 435

Number of ablations 2: 16

Attenuator setting 3 (%): 50

Depth 3 (nm): 435

Number of ablations 3: 12

Enter three measurements (attenuator %, measured total depths, and number of ablations). Depths will be divided by the number of ablations to obtain depth per hit.

Results

Radius (cm)	0.0125
Area A (cm²)	0.0006942
Fluence factor k	1
Slope S (nm)	38.123243
Threshold F_{th} (J/cm²)	0.279776
Target fluence F_t (J/cm²)	0.318985
Target energy E_t (µJ)	221.439239
Suggested attenuator (%)	22.1439
Save results	Save results to .txt

Figure 4: The calibration calculator in the Knowledge View tool of Avantage Software.

Conclusion

Femtosecond laser ablation offers many advantages for XPS depth profiling, including the ability to maintain sample chemistry throughout a depth profile, as well as the overall speed of the laser ablation. With the Hypulse Surface Analysis System, calibration of the ablation rate is straightforward and uses a simple calculation that is also conveniently incorporated into Avantage Software.

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