XPS depth profiling of coated nitrided steel using femtosecond laser ablation

Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful surface analysis technique that provides essential information about elemental composition along with chemical and electronic states. Depth profiling, a process in which material is repeatedly and sequentially analyzed with XPS and removed, provides access to buried features, layers, and interfaces. Traditional ion sputtering methods for depth profiling can, however, lead to preferential sputtering and chemical damage, impacting the reliability and accuracy of results. This is particularly problematic for complex, multi-layered structures and coatings, where it is crucial for the stoichiometry and chemical integrity to be maintained throughout the depth profile.

This application note explores the use of femtosecond laser ablation (fs-LA) as an alternative to conventional ion sputtering for XPS depth profiling. Specifically, this approach is used to analyze a nitrided steel surface coated with a titanium-doped molybdenum disulfide (MoS_2:Ti) layer, which was applied with physical vapor deposition (PVD). Nitriding is typically used in applications where durability is critical, such as in the production of gears, as it increases surface hardness and wear resistance. The addition of a MoS_2:Ti coating offers additional benefits such as enhanced lubrication and wear resistance. Molybdenum disulfide is well-known for its lubricating properties, and doping with titanium improves mechanical strength and adhesion to the substrate. Accurate depth profiling is essential for unraveling how these structures increase performance and for their further optimization and improvement.

Experimental

The sample is a heat-treatable steel, EN31CrMoV9, which underwent gas nitriding at 550°C for 120 hours to enhance its surface hardness and wear resistance. A 1.2 µm thick MoS_2:Ti coating was subsequently deposited using magnetron sputtering, which is a common technique for the production of hard coatings. Figure 1 shows a scanning electron microscopy (SEM) cross-section of the sample.

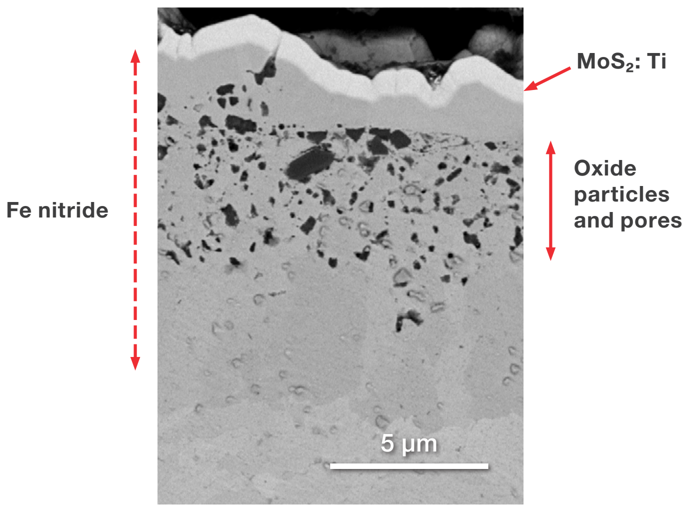

Figure 1. An SEM micrograph of the nitrided steel sample investigated in this application note, showing the MoS_2:Ti coating and iron nitride layer, rich in oxide particles and pores.

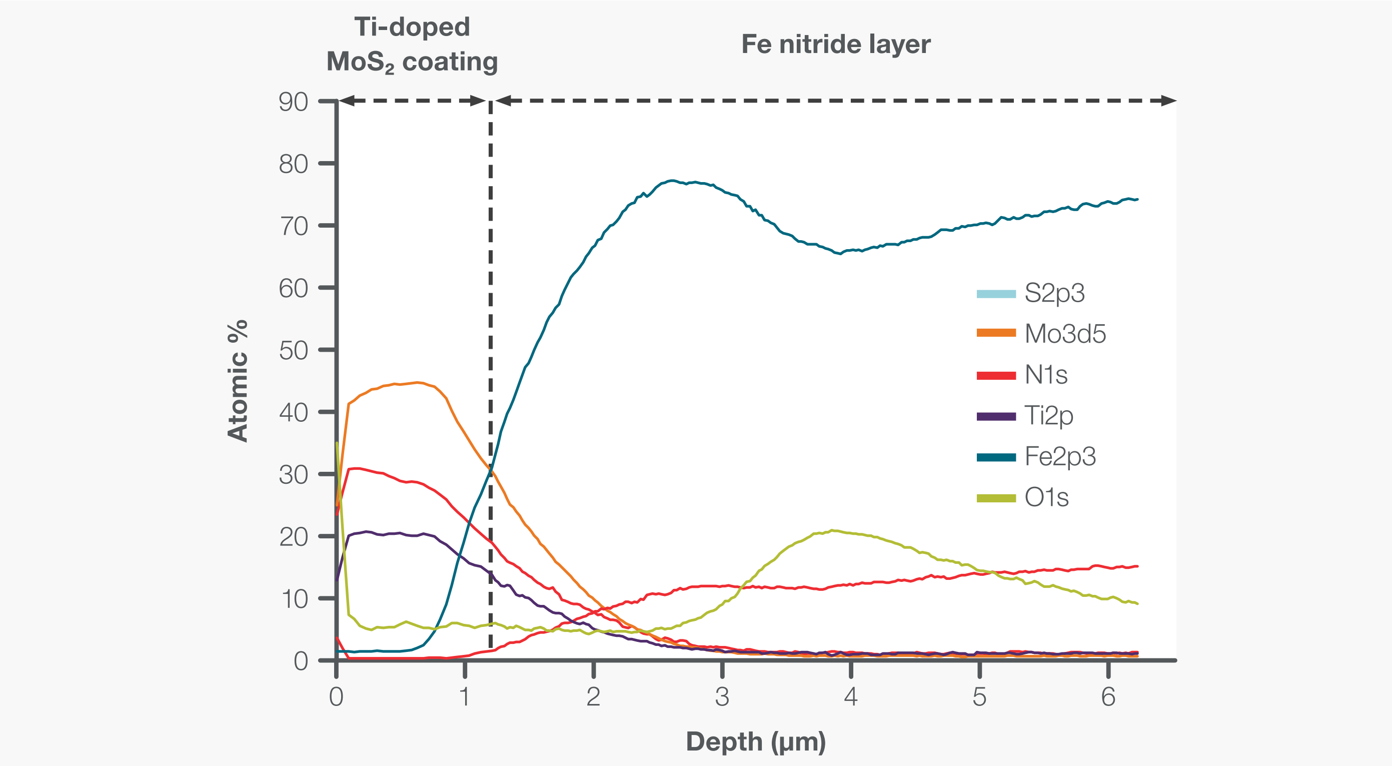

Figure 2. 500 eV Ar^+ depth profile of the nitrided steel sample, showing relative atomic percentages to an approximate depth of 6 µm.

A Thermo Scientific™ Hypulse™ Surface Analysis System, equipped with both traditional ion sputtering and fs-LA capabilities, was utilized for the analysis. XPS data was collected in SnapShot mode using a 30 µm X-ray spot size. A 500 eV monoatomic Ar^+ beam from a Thermo Scientific™ MAGCIS™ Dual Beam Ion Source was used for sputter depth profiling. The fs-LA depth profiles were generated using a 1,030-nm laser operating at a 160 fs pulse length. The pulse energy was increased from 83 µJ to 250 µJ when transitioning from the MoS_2:Ti coating into the bulk steel material.

Results

The Ar^+ ion-sputtering depth profile is shown in Figure 2. The MoS_2:Ti coating composition was found to be $(Ti, Mo)_{0.5}$, which deviates significantly from the expected stoichiometry. This is likely due to a preferential removal of sulfur. Chemical damage was also evident from shape and positional changes to the Mo3d, Ti2p and S2p peaks (spectra not shown). In contrast, the fs-LA depth profile (Figure 3) preserved the stoichiometry of the MoS_2:Ti coating more accurately. The composition at the center of the coating yielded a stoichiometry of $(Mo, Ti)S_{1.8}$, closely matching the expected value. Peak binding energies of Mo3d, Ti2p, and S2p remained consistent, also indicating minimal chemical changes and preferential sputtering.

For the iron nitride layer, the fs-LA depth profile showed Fe_xN stoichiometries in the range of $Fe_{2.5\text{-}3.2}N$, closely matching glow-discharge optical emission spectroscopy (GDOES) results ($Fe_{2.8\text{-}3.3}N$, not shown). However, the ion sputtering profile showed much higher Fe:N ratios ($Fe_{6.4\text{-}7.9}N$), indicating significant preferential sputtering of nitrogen. These findings align with Rietveld analysis of X-ray diffractograms (not shown), which confirmed the presence of ε-phase ($Fe_{2\text{-}3}N$) and γ'-phase (Fe_4N) in the compound nitride layer. The fs-LA and GDOES results are consistent with the expected stoichiometry from X-ray diffraction, while the ion sputtering results appear to deviate due to preferential sputtering of nitrogen and oxygen.

Additional benefits of fs-LA depth profiling include a reduced experiment duration along with an increased potential sampling depth. For instance, in the case of the above sample, the total experiment time that the laser profile took to reach an ~11 µm depth was approximately 7 hours, which primarily consisted of XPS analysis time. The ion beam method took over 30 hours to reach about half this depth, where approximately 65% of that time was devoted to sputtering.

Notably, it is also possible to tune laser parameters throughout the analysis of thicker layered materials to obtain depth and interface resolutions comparable to those of convention ion beam profiling. This is indicated by the similar profile structures shown in Figures 2 and 3.

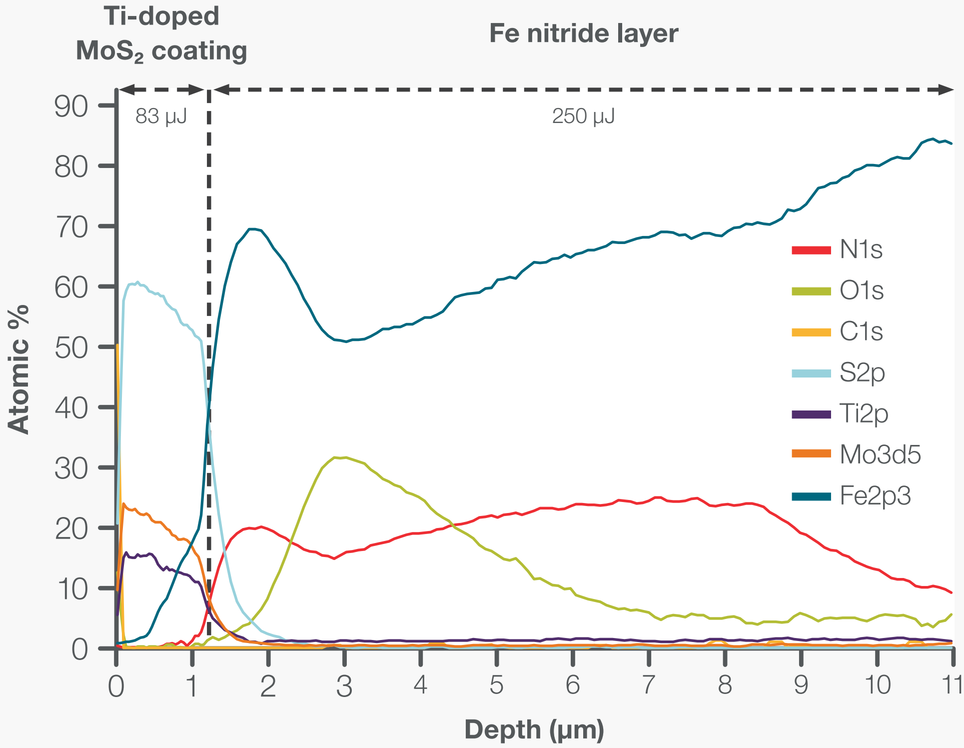

Figure 3. fs-LA depth profile of the nitrided steel sample, showing relative atomic percentages to an approximate depth of 11 µm.

Summary

XPS depth profiling with femtosecond laser ablation offers a robust alternative to traditional ion sputtering, particularly for materials sensitive to preferential sputtering and chemical damage. The technique provides accurate stoichiometric analysis and preserves chemical state information, making it ideal for complex, multi-layered structures with deeply buried interfaces. The fs-LA method can offer comparable depth resolution to ion sputtering while being able to profile greater depths in a fraction of the time.

This application note demonstrates the effectiveness of fs-LA in maintaining the chemical integrity of a nitrided steel material with a MoS_2:Ti coating throughout a depth profile, providing accurate and reliable results in a practical timeframe.

Acknowledgement

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Reference

1. Baker, MA, et al. **Femtosecond laser ablation (fs-LA) XPS – A novel XPS depth profiling technique for thin films, coatings and multi-layered structures.** *Applied Surface Science 654* (2024). doi: 10.1016/j.apsusc.2024.159405

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