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Feasibility of depth profiling of Zn-based coatings by laser ablation inductively coupled plasma optical emission and mass spectrometry using infrared Nd:YAG and ArF* lasers[☆]

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Abstract

The feasibility of depth profiling of zinc-coated iron sheets by laser ablation (LA) was studied using an Nd:YAG laser (1064 nm) with inductively coupled plasma optical emission spectrometry (ICP-OES), and an excimer ArF* laser (193 nm) with a beam homogenizer. The latter was coupled to an ICP with mass spectrometry (ICP-MS). Fixed-spot ablation was applied. Both LA systems were capable of providing depth profiles that approach the profiles obtained by glow discharge optical emission spectroscopy (GD-OES) and electron probe X-ray microanalysis (EPXMA). For Nd:YAG laser an artefact consisting of zinc depth profile signal tailing appeared, enlarging thus erroneously diffusional coating–substrate interface profile. However, the ArF* system partially reduced but not suppressed that phenomenon. For both LA systems the Fe signal from the substrate increased with depth as expected and reached a plateau. The depth resolution (depth range corresponding to 84%–16% change in the full signal) achieved was several micrometers. Ablation rate was found to depend on ablation spot area at constant irradiance. Consequently, ablated volume per shot dependence on pulse energy exhibits deviation from linear course.

Keywords: Laser ablation; Inductively coupled plasma; Atomic emission spectrometry; Mass spectrometry; Depth profiling; Zinc coated sheet

1. Introduction

In recent years a choice of instrumental analytical methods became available to carry out depth profile analysis on solid surfaces. Depth profiling of layers in nanometer and sub-micrometer scale is mostly accomplished by using X-ray photoelectron spectroscopy (XPS) [1–4], Auger electron spectroscopy (AES) [2,4], secondary ions (neutrals) mass spectrometry (SIMS, SNMS) [4], sputter-assisted electron probe microanalysis (EPXMA) or total reflection X-ray fluorescence spectrometry (TXRF) [5], XPS combined with chemical etching or ion sputtering [6].

Quantitative depth profiles in the range from tens of nanometers to tens and hundreds of micrometers are nowadays routinely obtained by means of glow discharge optical emission spectroscopy (GD-OES) [7,8]. Various modifications of this technique may result in extraordinary depth resolution of 1 nm [9]. Elements such as hydrogen, nitrogen and oxygen may be also determined by GD-OES because of the isolation of the excitation space from the ambient atmosphere. [10].

Similar to photon probe/electron probe techniques, solid sample vaporisation by means of focused laser beam allows performing local analysis/microanalysis [11,12]. The laser ablation (LA) based spectroscopy is accomplished either by coupling of a LA device as a generator of aerosol with inductively coupled plasma atomic emission (or mass) spectrometry (LA-ICP-AES, LA-ICP-MS) [13] or by

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detection of photons emitted by atomized sample constituents in laser-induced plasma (laser-induced breakdown spectroscopy—LIBS) [14]. With LA-based techniques, the depth profiling in micrometer range (from X μm to 0.X mm) is feasible, too.

Contrary to GD-OES and photon/electron/ion probe techniques, LA-based spectroscopy techniques are routinely operated under atmospheric pressure. Although the resulting simple manipulation makes the LA-based techniques promising tools for direct solids analysis, there are still drawbacks that hamper their applications explicitly in depth-profile analysis. Application of LA-ICP-MS in the depth profiling of multi-layer perovskite structures of 300–500 μm total thickness has been reported [15]. The authors concluded that LA-ICP-MS was a good compromise between depth resolution and depth quantification. The influence of the magnitude of irradiance on the depth profile characterization by LIBS was studied in Ref. [16] and optimized conditions were applied in the depth profile analysis of metal jewels [17].

The correspondence between a sample elemental depth-profile obtained by using a LA-ICP-OES/MS and the real in-depth distribution of constituents depends on the wavelength, pulse width and pulse energy of employed laser, the form of the laser energy distribution over the beam cross-section, the focusing optics, the laser beam imaging onto the target, ablation chamber shape and volume, transport tubing dimensions and material, carrier gas and detector characteristics. Lasers with cylindrical resonators produce Gaussian beams due to the character of the electromagnetic field distribution inside the resonator [18]; however, the beam profile may be partly distorted [19]. The laser mirrors are often adjusted to produce so-called super-Gaussian (top-hat) beam profile [20]. A single-lens focused Gaussian beam produces a crater which becomes narrower with increasing depth. Consequently, each laser shot removes material not only from the crater bottom but also from crater walls, where the irradiance is still sufficient to bring about vaporization. Decreased in-depth resolution follows from this geometry of interaction. The ablation crater model proposed by St. Onge [20] is based on a Gaussian beam profile assumption and predicts ablation behaviour in good agreement with experimental observations, although the real beam-target interaction effects surpass this model. Frequently observed fractionation of elements in ablation-produced aerosol prior to its transport is a result of selective vaporization. A crater depth-to-diameter ratio plays an important role in the fractionation, which is significantly reduced when this ratio is < 6 [21,22].

Ablation experiments are usually performed by using a beam focused few millimetres behind or above the sample surface [16]. Therefore, energy profile of unprocessed laser beam may not fulfil requirements on ablation crater shapes needed for depth profile analysis. In order to improve the cross-section energy distribution, various beam homogenizing procedures have been developed. A double lens-array based beam homogenizer applied for depth profiling by Bleiner et al. [23] produces craters with nearly flat bottom. In spite of the flat-top profile the beam is consequently focused conically by Schwarzschild objective as a frustum. This degrades the advantage of the homogenized profile. For comparison, ablation craters produced by a laser with a Gaussian beam profile narrow with depth and exhibit curved (convex) walls and a concave bottom. The shape can be described mathematically [20]. In addition to the crater geometry, the ablation processes give rise to rims of deposited material with modified stoichiometry which may be re-ablated. The massive deposition can be diminished by using helium instead of argon as the carrier gas [24,25]. As a result of the above mentioned phenomena related to crater formation, the signal of the upper layer overlaps in some cases the signal of the substrate excessively. This “tailing” is considered to be an artefact which is proved by comparison with ”true” depth profiles obtained e.g. by GD-OES. It is mainly caused by the ablation of conical crater walls and deposited material surrounding the crater mouth [20–22,24,25]. Vadillo et al. [26] used a two-lens telescope in order to narrow the laser beam for higher irradiance instead of a single-lens focusing the beam conically. The irradiance 10^7 W cm^{-2} was lower than the typical values used for ablation ($> 10^9$ W cm^{-2}) but yet sufficient for efficient depth profiling of zinc coated iron sheet.

Nanosecond laser pulses (FWHM = 4.4 ns for Nd:YAG) and the near infrared radiation (1064 nm) cause the thermal effects to be significant with regard to true ablation and melting of the target material in the depth region of micrometers occurs [27]. In spite of the differences between the IR and UV ablation mechanisms, the effect of the nanosecond pulse is common to both IR and UV (FWHM = 15 ns for ArF* 193 nm) laser ablation systems. The mechanism is rather similar to the continuous melting, which creates analogous craters [27,28].

The aim of this work was to evaluate and compare quality of depth profiles (depth resolution, signal tailing, ablation rate) which were obtained using two different laser ablation systems on zinc coated iron sheets. The profiles were also compared with those yielded by GD-OES and EPXMA with energy dispersive X-ray spectrometry (EDX). The experiments were aimed at indicating to what extent the LA systems would be able to approach the “true” depth profiles measured with the established methods GD-OES and EPXMA.

2. Theoretical depth profile considerations

The key parameter for depth profile analysis is depth resolution. Depth resolution of laser ablation depth-profiling technique is defined for a sharp interface as a depth interval Δz, for which the signal of the constituent (element) A in the first (upper) layer diminishes with increasing depth from 84% of its plateau value in the first layer to 16% and the signal of the element B in the second (lower) layer increases from 16% to 84% of its plateau value in the second layer