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Technical note

Depth profiling of nanometer thin layers by pulsed micro-discharge with inductively coupled plasma mass spectrometry

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ABSTRACT

A depth profile technique has been developed for ultrathin layer analysis by combining a pulsed micro-discharge device with inductively coupled plasma mass spectrometry (ICPMS). With a tungsten needle as the anode and the sample as the cathode, a local micro-plasma was formed in the 50 μm discharge gap, which contributed to the ablation of the sample. We analyzed a series of Ni coating samples with thicknesses of 5, 10, 15, and 20 nm in this study. Although the micro-discharge was shown to be an arc, pulsed mode operation provided an extra control over the power output and the discharge time that enabled precision ablation of submillimeter in lateral scale and 0.6 nm in depth per pulse. A further attempt was made to demonstrate the ability in thickness determination using the calibration curve for layers of different thicknesses. Our results show that the pulsed micro-discharge could directly ablate a solid sample under ambient conditions and that it is an effective low-cost method for depth profiling of nanometer thin layers.

1. Introduction

With the rapid development in material and surface science, thin layers of different compositions and thicknesses are used in a wide range of applications. It is important to perform a depth profile analysis of thin layers using highly sensitive techniques that can achieve high depth resolution but are low cost and efficient to meet the increasing demand for routine analysis.

Various techniques have been developed for ultrathin layer analysis, providing flexibility and feasibility to satisfy the diverse analytical requirements. Depth profile analysis can be accomplished with secondary ion mass spectrometry (SIMS) [1,2] and X-ray photoelectron spectroscopy (XPS) [3,4]. Lateral and depth resolution at the nanometer range have been achieved. However, both methods require high vacuum, expensive instruments, and long analysis times. Glow discharge-based techniques such as glow discharge optical emission spectrometry (GDOES) and glow discharge mass spectrometry (GDMS) are powerful tools that can be applied to depth profile analysis of layers over a very wide thickness range (from tens of nanometers to tens of micrometers) [5]. However, limitations exist, such as the low operating pressure, specific requirements for sample shape and dimensions, and poor lateral resolution. Compared with the techniques mentioned above, laser ablation inductively coupled mass spectrometry (LA-ICPMS) is more popular and has been successfully applied in many areas [6,7]. LA-ICPMS provides spatially resolved information at a lateral resolution of a few micrometers using an LA cell operating under ambient conditions. Nevertheless, the analysis of nanometer thin layers is a challenging task because the minimum penetration depth per shot is commonly dozens of nanometers even if a femtosecond laser is employed.

Atmospheric-pressure (AP) discharge has attracted considerable attention in past decades due to its convenient operation at AP and the low cost of the equipment. In analytical chemistry, spark ablation combined with inductively coupled plasma mass spectrometry (SA-ICPMS) or atomic emission spectrometry (SA-ICPAES) has been successfully applied for the bulk analysis of alloy steels [8], ferrovanadium [9], and automotive catalytic converters [10], and there are several reports illustrating an arc nebulization technique used for elemental analysis [11,12]. These techniques have already proven to be efficient in the field of direct solid analysis. However, the application to thin layer analysis is particularly rare even though SA-ICPAES is commercially available. Conventional spark ablation, which is conducted between a rod electrode and a conductive sample separated by several millimeters, randomly wanders over the sample surface; a large spot diameter of several millimeters is unavoidable [13]. The arc is so intense that severe melting and the evaporation of the electrode material occur, resulting in uncontrollable damage to the sample surface. It has been reported that arc or spark ablation cannot be used for accurate spatially resolved analyses [14].

In the present study, an easy-to-operate needle-plane micro-discharge device was designed and applied as an ablation source coupled to ICPMS. The traditional rod electrode in spark ablation was

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altered to a tungsten needle, and the tip-to-sample distance was shortened to 50 μm. The discharge was operated in the pulsed mode with adjustable voltage magnitude, pulse width, and frequency, which offered excellent flexibility for regulating the discharge and allowed a well-controlled ablation rate. This study explored the depth profile analysis of Ni coatings for layers of varied thickness. Indexes for the evaluation of the analytical capability including the ablation rate and depth resolution are discussed. A calibration curve is presented to demonstrate the quantitative ability for thickness determination. Finally, the novelty of using microsecond pulse width is emphasized.

2. Experimental

Fig. 1 shows the schematic diagram of the entire system. A cell built in-house was used to form ablated species via a micro-discharge, and then, the species were transported through a tube to the ICPMS. The micro-discharge cell (4 cm^3 volume) contained a tungsten needle, a sample, and a quartz cylindrical chamber. The tungsten needle tip was fabricated by an electrochemical method [15] using tungsten wire (99.9999%) with a diameter of 250 μm (Xiamen Tungsten Ltd, Xiamen, China) for the anode. A pulsed high voltage power supply (SY3002, Senyuan Technology Co., China) with an output voltage of 0–5 kV and a pulse width of 1–10 μs was connected to the anode to ignite and maintain the discharge. An image of the micro-discharge is shown in Fig. 2. The sample, which acted as the cathode, was placed on a micrometer stage. N_2 (99.99%) was employed as the work gas, carrying the ablated species from the cell to the ICPMS (Model 4500, Hewlett-Packard) through a Teflon tube (50 cm in length, 4 mm i.d.). The flow rate of N_2 was maintained at 50 mL/min by a mass flow controller because a higher flow rate would quench the ICP plasma. The entire cell was airtight to guarantee that the discharge occurred in N_2. The electrical parameters of the discharge were acquired via an oscilloscope (WaveSurfer422, Lecroy, USA) with a high voltage probe (PPE 6 kV, Lecroy, USA) and a current probe (TCP202, Tektronix, USA). A CCD camera was mounted in front of the ablation cell for observation. The tip-to-sample distance was maintained at ~50 μm. The typical operating parameters of the micro-discharge cell and the ICPMS are listed in Table 1.

Samples with Ni layer of 5, 10, 15, or 20 nm in thickness were deposited by a radiofrequency magnetron sputtering device (JC-500-3/D, Vacuum Machinery Plant, China) from a pure Ni target onto Ta substrates (Orient Tantalum Niobium Co., China). During the sputtering process, the chamber pressure was maintained at 1.5×10^{-3} Pa while the Ar gas flow was fixed at 100 sccm. The target-substrate distance was 8 cm. Under these conditions, the deposition rate at the substrate surface was 0.1 nm/s. Thus, thin layers with variable and well-controlled thickness in the nanometer range could be deposited by changing the deposition time. In addition, low alloy steel (GBW01400) obtained from the Chinese National Standards Center was chosen to evaluate the ablation capability of the micro-discharge.

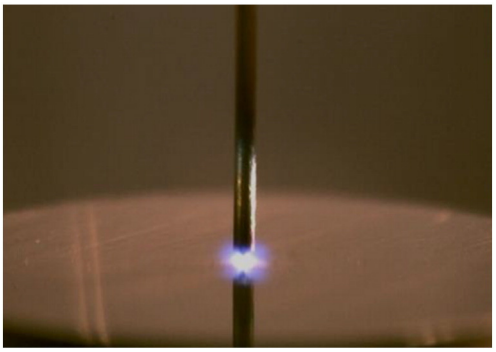

Fig. 2. Image of the micro-discharge.

3. Results and discussion

To understand the ablation mechanism, the voltage and current profiles with a 2 μs pulse width were acquired. As shown in Fig. 3, the voltage dropped rapidly accompanied by an increase of the current up to 28 A, suggesting a quick transition to the arc after the discharge was ignited. In the arc, there is an abrupt drop of field and potential in a very thin layer in front of the cathode (i.e., the cathode sheath), which is thought to be free of collision [16]. Electrons emitted from cathode are accelerated to a considerable energy in this collision-free sheath and subsequently ionize the species in the cathode region, yielding a large number of ions. These ions, carrying the kinetic energy acquired in cathode sheath, will subsequently sputter the electrode material and give rise to the ablation of the sample surface [17]. Although it has been shown to be an arc, this pulsed needle-plane discharge is more similar to a laser in terms of the frequency and deposition energy. The deposition energy is approximately 4.5 mJ per pulse, which is equivalent to the laser energy applied in LA-ICPMS [6,18].

As the plasma gas used in an ICP torch, Ar without doubt has the priority over N_2 to be the discharge gas in the arc. However, compared to Ar, N_2 has a higher specific heat and thermal conductivity, which makes the plasma more compressed. The compressed plasma leads to a decrease in the arc diameter [19]. Moreover, due to the reduction of

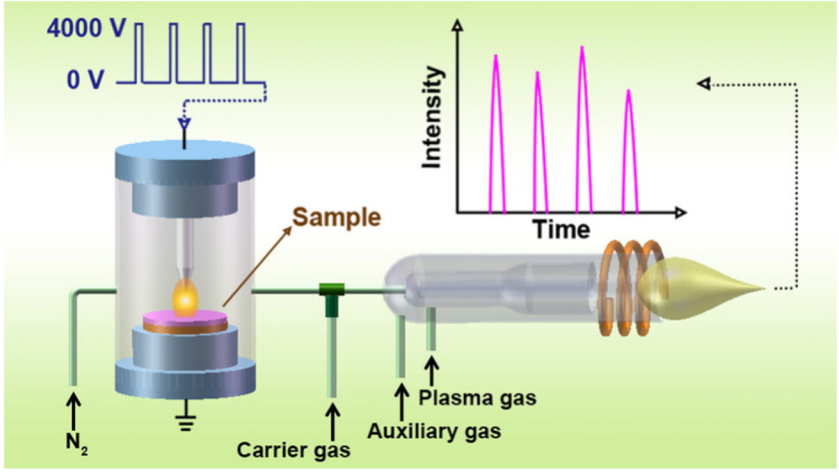

Fig. 1. Schematic diagram of the micro-discharge cell coupled to an ICP torch.