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Spark ablation–inductively coupled plasma optical emission for elemental depth profiling and imaging

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ABSTRACT

Spark ablation was coupled to inductively coupled plasma-optical emission spectrometry (ICP-OES) for direct solid sample introduction. The preliminary applications including elemental depth profiling of metallic thin films and surface elemental imaging for solid conductive samples were explored to expand the applications of traditional ICP-OES. The parameters affecting the spark discharge for ablation sampling including electrode materials, electrode gap, discharge voltage, and gas flow rate were investigated in details. The mechanism of spark ablation was also briefly discussed with data of X-ray photoelectron spectroscopy.

1. Introduction

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is widely used for trace element determination for its unique advantages, such as multi-element capability, wide linear dynamic range, high sensitivity and high sample throughput [1,2]. Because of its importance for atomic spectrometry, sample introduction to ICP has long been a hot research topic in analytical atomic spectrometry. Aqueous solutions make up the majority of final samples measured by ICP-OES, and a large number of sampling modes have been evolved for liquid samples, such as pneumatic nebulization [3–6], ultrasound nebulization [7–9], thermospray [10–12], chemical vapor generation [13–15], photochemical vapor generation [16,17], and dielectric barrier discharge induced vapor generation [18,19]. However, direct solid sample analysis without any prior dissolution would be clearly advantageous, since most samples are solid ones. In fact, it has also been widely used in early optical emission spectrometry, for example, direct powder sampling [20,21], DC arc discharge sampling [22] and spark ablation sampling [23,24]. The hotspots of solid sampling for ICP-OES have been mainly focused on the powder sample introduction [25–27] and laser ablation [28,29] in recent years.

Electrical discharge machine (EDM), especially the spark discharge, has obtained wide applications in metallic material cutting and fine processing [30], electro-spark deposition [31], synthesis of nanomaterials [32,33], and so on. In analytical chemistry, spark discharge-optical emission spectrometry (SPARK-OES) has also been applied in rapid metal analysis due to its direct collection of spectral signals generated in electrical spark excitation [34,35]. However, direct SPARK-OES needs a well designed precise optical system to acquire the resultant spectral data. Because of the coexisting dissociation capability of spark discharge, an electrical spark is often connected with a subsequent excitation/ionization source as a sample introduction tool, for example, a mass spectrometer [36–38]. Similarly, coupling of spark discharge to ICP-OES would retain advantages of both.

With the development of material science, elemental analysis of thin films gains a growing demand, which includes not only the average content of elements but also their spatial distribution, for example, depth profiling analysis and elemental imaging of samples. Traditional methods such as micro-X-ray fluorescence spectroscopy (MXRF) [39], scanning electron microscopy-energy dispersive spectroscopy (SEM-EDX) [40], secondary ion mass spectrometry (SIMS) [41] and X-ray photoelectron spectroscopy (XPS) [42] could be used for this purpose. However, the high vacuum requirement and often high instrumental cost could restrict their popularity. Recently, Zhang et al. [43] have studied the depth profiling of nano-coatings by coupling a low-temperature plasma probe with an inductively coupled plasma-mass spectrometer. Surface morphological and elemental spectral imaging of conductive samples has also been explored with pulse spark discharge optical emission spectrometry recently in our research group [35].

In this work, a micro spark discharge (MSD) ablation device was constructed and used for direct solid sampling to an ICP-OES system. Using this MSD-ICP-OES, depth profiling analysis of single layer and

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multilayer metallic film samples, and elemental spectral imaging for planar conductive samples were briefly explored. It is an attempt to expand the applications of traditional ICP-OES and could be a foundation for further three-dimensional elemental imaging.

2. Experimental

2.1. Instrumentation

In this work, an ICP-OES system (ARCOS FHS12, SPECTRO Analytical Instruments Inc., Germany) was used for atomic emission signal excitation and acquisition as well as data processing. Fig. 1 is the schematic diagram of main device for solid sample ablation introduction into ICP-OES. The micro-spark discharge unit for elemental depth profiling and parameter optimization is shown in Fig. 1A. Two perpendicular and intersected holes (i.d. 5 mm) were made through a Teflon base, and a cavity was automatically formed at the intersection. The pair of horizontal holes was used to fix the two electrodes, with a distance gap of about 1 mm appropriately at the center of the cavity. One electrode was served as the working electrode with a needle tip end using a tungsten rod. The other is the copper rod with a flat end; it also served as the substrate on which the thin films of different materials were coated as samples alternatively. The two electrodes were connected to an AC high voltage power supply (CTP-2000 K, Nanjing Suman Electronics Co., Ltd.), with a transformer for adjustable voltage input to obtain required high voltage output for discharge. Another pair of holes in the vertical direction was used for the inlet and outlet of the working gas from bottom to top; the lower one was for the gas input, while the upper one was for its output, which was also connected to the ICP torch. Ablated solid sample aerosols were transported into the ICP for excitation and generation of atomic and/or ionic spectral lines for optical detection. The RF power for ICP-OES was 1400 W, the vertical viewing height was 15 mm, and the flow rates of cooling and auxiliary gas were 12 L min^{-1} and 1 L min^{-1}, respectively.

For elemental imaging analysis of a planar conductive sample, the design of spark discharge unit was fine tuned, as shown in Fig. 1B. The sample electrode was replaced with the planar conductive sample immobilized on a Teflon substrate, which was fixed on a manual two-dimensional linear stage (LGY 60-L, Dongguan Sheng Ling Precision Machinery Co., Ltd., China). Thus, a point-surface discharge with adjustable discharge spot was formed between the needle tip working electrode and the sample plate. To ensure transporting the ablated sample into the ICP effectively, the sample surface should be flat enough to tightly fit the spark ablation device and seal the discharge cavity.

The metallic thin films on copper substrate were deposited by a magnetron sputtering system (JGP450, Scientific Instrument Development Center of Shenyang, Chinese Academy of Sciences). The film thickness was measured by a surface profiler (XP-2, Ambios Technology, Inc., USA). The electrical parameters of the discharge were tested with a digital oscilloscope (TDS 2024C, 200 MHz, Tektronix, USA).

2.2. Reagents and materials

The materials with a purity of 99.99% including Al, Cu, Ti and W purchased from local market were used for electrodes, all in form of rods with a diameter of 2 mm. The working end of Cu electrode was polished and coated with Al, Ni or/and Zn films (Al and Zn: 5 N, Williams Advanced Materials, USA; Ni: 5 N, Beijing Ximengtai Trade Center, China) as the samples for depth profiling analysis. A rectangular copper foil with an inlaid "V" shaped Al foil was used for test of elemental imaging.

2.3. Analytical procedure

The working and sample electrodes were all polished with 1000 mesh metallographic sandpaper and cleaned with alcohol cotton, and followed by air blow-dry prior to discharge. The high voltage power supply was firstly switched on, and an appropriate discharge voltage was adjusted through the transformer to generate the required spark discharge between the working and sample electrodes. The ablated sample aerosols were transported into the ICP by the argon working gas for excitation of atomic emission signal and optical detection, and the temporal spectral data of multi-wavelength were recorded simultaneously. Through monitoring specified elemental spectral emission lines, elemental depth profiling would be achieved; moreover, elemental imaging of the sample surface could be also achieved by administrating XY coordinates on the two-dimensional linear stage to realize sample surface scanning.

3. Results and discussion

3.1. Selection of electrode

The shape of working end of electrodes would affect the discharge characteristics. In this work, the parallel round end and needle tip end of electrodes were tested. And the former would result in igniting the discharge at the edge of electrodes, with uncontrollable and unpredictable discharge spot. Therefore, a final needle-to-plate type spark discharge mode was used in order to limit the discharge spot for precise arrangement, which was also convenient for better spatial resolution of subsequent imaging analysis. In fact, the generation of nano-aerosols using this structure has also been reported [44].

Four types of materials for needle tip working electrode including Cu, Al, Ti and W with a flat Cu electrode in the needle-to-plate spark discharge generators were compared, respectively. After continuous discharge for about 20 min, it was found that the Cu needle tip electrode

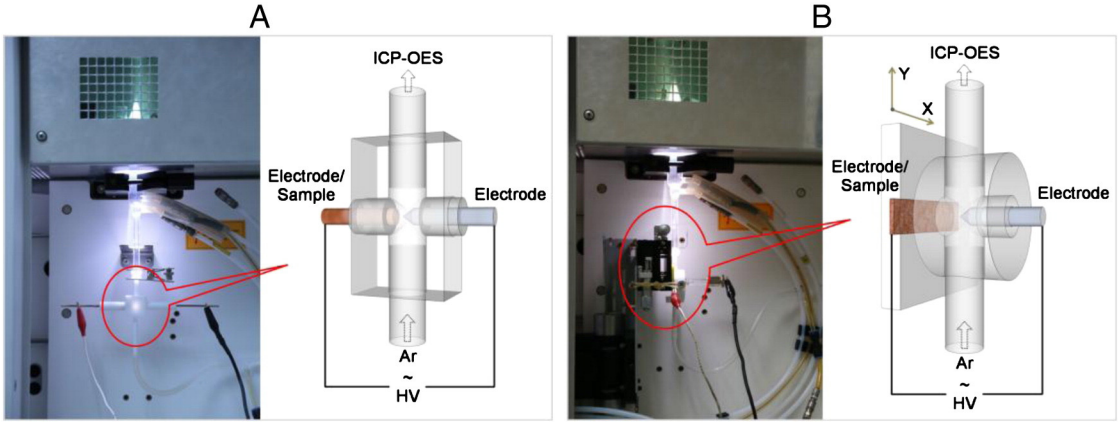

Fig. 1. Schematic diagram of micro-spark ablation device sampling for ICP-OES system. (A) Elemental depth profiling and (B) elemental imaging.