



# Surface morphological and elemental imaging by low power atmospheric pulsed spark discharge optical emission spectrometry



Yunfei Tian<sup>a,b</sup>, Xi Wu<sup>b</sup>, Xiaoming Jiang<sup>b</sup>, Xiandeng Hou<sup>a,b,\*</sup>

<sup>a</sup> College of Chemistry, Key Laboratory of Green Chemistry and Technology of MOE at Sichuan University, Chengdu, Sichuan 610064, China

<sup>b</sup> Analytical & Testing Centre, Sichuan University, Chengdu, Sichuan 610064, China

## ARTICLE INFO

### Article history:

Received 2 March 2013

Accepted 12 March 2013

Available online 20 March 2013

### Keywords:

Elemental imaging

Morphological imaging

Spark discharge

Optical emission spectrometry

Alloy

## ABSTRACT

A new surface morphological and elemental imaging system was built by using low power atmospheric pulsed spark discharge optical emission spectrometry (PSD-OES). This PSD-OES can well excite atomic lines of iron, chromium, zinc, copper and more. Optical emission intensity is affected by the distance between electrode and sample surface significantly when the electrode is very close to sample, enabling the surface morphological imaging possible for some samples such as a coin. For a roughly flat surface sample, when the distance is set at about 0.5 mm, the optical emission intensity is insensitive to tiny distance change, thus elemental imaging is possible. As an example, zinc stripes on copper plate can be well recognized by this elemental imaging technique, with a spatial resolution about tens of micrometers, which can be further improved by minimizing the optical aperture. A significant advantage of this technique is that it can obtain information at a series of specific wavelengths from a signal experiment for multi-element imaging.

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## 1. Introduction

Optical emission spectrometry using various discharges has been frequently used to directly obtain elemental composition of solid samples without a complicated pre-treatment procedure, so it can be suitable for surface elemental imaging [1–6]. Glow discharge (GD) has been one of the main modes for the study of discharge optical emission in the field of imaging analysis [7–9]. Winchester and Salit [10] obtained millimeter scale spatial resolution elemental composition images on an improved device capable of sustaining multiple discharges simultaneously. Hoffmann and Ehrlich [11] used an 8 mm diameter sputter crater as sample with inhomogeneity simulating function and observed the distribution of emission from a dc GD. They found that the species of the sputtering gas and its impurities show a constant distribution over nearly the whole excitation area, and the copper powder pressed into an iron plate was recognized by the copper emission peak.

Generally, a GD for elemental imaging works in a continuous mode. Webb et al. [3] coupled a dc GD to a monochromatic imaging spectrometer to obtain surface elemental images via optical emission spectrometry. The monochromatic imaging spectrometer was composed by a collection lens to collimate optical emission from the source, a monochromator to split light, a second lens to refocus the

collimated light at the selected wavelength onto a camera. The result is a monochromatic image of the source. The GD working in pulsed mode improved spatial resolution greatly as opposed to running the discharge continuously. This phenomenon was deduced to be the result of excitation of atoms in a limited discharge region in the case of pulse mode, 100 μm spatial resolution was obtained in their case [3]. When the discharge runs continuously, the sputtered analyte is allowed to diffuse throughout the plasma, thus emitting far from its original position and causing a loss in surface spatial information. What's more, a continuous mode GD has a disadvantage that only electrically conductive samples can be analyzed. In 2007, Gamez et al. [4] used a pulsed radio frequency GD to perform elemental imaging on insulating samples including proteins on blotting substrates, photographic film and glass. Among many discharge modes, a GD offers a broad dynamic range, low limits of detection, multi-elemental simultaneous analysis, and nanoscale depth profiling [9]. However, a GD usually requires relatively complicated instrumentation and the discharge region is difficult to be restricted in a specific scope [5,12].

The aim of the present study is to explore the possibility to use low power atmospheric pulsed spark discharge optical emission spectrometry (PSD-OES) for two-dimensional surface elemental and morphological imaging on solid samples. The operating parameters of the spark discharge including distance between the electrode and the sample surface and the discharge voltage were investigated in detail, because they obviously affected the discharge stability and the optical emission intensity. As examples, pure copper plate, zinc stripe on copper plate (Zn/Cu plate) and coin were analyzed with this new instrumental setup, with reasonably good results of elemental distribution and the surface morphology.

\* Corresponding author at: Analytical & Testing Center, Sichuan University, Chengdu 610064, China. Tel.: +86 28 85470818.

E-mail addresses: [houxd@scu.edu.cn](mailto:houx@scu.edu.cn), [houxiandeng@yahoo.com.cn](mailto:houx@scu.edu.cn) (X. Hou).

## 2. Materials and methods

### 2.1. Installation

In this work, imaging is performed by scanning the sample surface with the discharge, while the optical emission is detected by a charge coupled device (CCD) spectrometer, as depicted in Fig. 1a. The spark discharge consists of an electrode (Pt/Ir wire, Shanghai NTI Co., Ltd., Shanghai, China), a sample holder (an iron plate on stage) and a power supply composed with a regulator (TDGC2-1, 0–250 V, 1 kVA, Huyu Group Co., Ltd., Wenzhou, China) and a plasma generator (CTP-2000K, 0–30 kV, 1–100 kHz, Suman Electronics Co., Ltd., Nanjing, China). The plasma generator supplies pulsed voltage between the electrode and the sample to produce a discharge and to ablate and excite analyte atoms from the sample surface. The scanning is performed by moving sample at two dimensions with a motorized precise (1 m) positioning stage (SCAN 75 × 50, Märzhäuser GmbH,

Wetzlar, Germany). The electrical parameters of the discharge can be tested by a digital oscilloscope (TDS 2024C, 200 MHz, Tektronix).

The optical detection system contains an objective lens (MPLN10X, Olympus, Japan), an aperture (0–1000 μm adjustable), a group of reflective mirror, a grating (600 gr/mm), a CCD spectrometer (Synapse, Horiba Jobin Yvon, Edison, NJ) and a computer. The emission light from the discharge region was collected by the objective lens, goes through the aperture and mirrors, and reaches the grating. After dispersion according to wavelength by the grating, light intensities of different wavelengths were recorded by the CCD and saved in the computer. The identification of emission peaks was accomplished by comparing the emission wavelengths with the reference data [13].

### 2.2. Samples

Samples include a pure copper plate, a Zn/Cu plate and a coin. The pure copper plate was 99.999% from Huludao Zinc Plant, Huludao, China. The Zn/Cu plate was prepared with pressing some zinc stripes (99.90%, Chengdu Jinshan Chemical Reagent Co., Ltd., Chengdu, China) into a copper plate mentioned above. The coin sample was a ten-cent coin of Renminbi (a Chinese coin, stainless steel, 2011). We selected the back pattern (orchid flower) of the coin for use in this work.

### 2.3. Emission processes of PSD-OES

Fig. 1b illustrates the optical emission processes of PSD-OES. The discharge produced by the high voltage between electrode and sample etches the sample and causes sample atom release. These atoms are excited by the plasma in discharge region and release photons which come from atomic emission processes. To the different components, the atomic emission spectra are the characteristic corresponding to elements. Recording atomic emission spectra along with sample movement, an array of every point atomic emission spectrum is formed, in other words, an image of element is accomplished.

## 3. Results and discussion

### 3.1. Spectral characteristics

We previously found that a corona discharge (CD) operating in a pulsed mode can dissociate volatile organic compounds (VOCs) and excite the free radicals dissociated in the processes [14]. However, atomic emission of solid samples needs more energy to free atoms from bound states which is confirmed by the absence of atomic lines in the CD mode. Along with increasing the discharge voltage, the CD is converted to a spark discharge (peak voltage: ~1650 V, and peak power: ~0.5 W) with obvious light emitting and sounding. Fig. 2 shows the emission spectrum of the copper plate at 1800 V discharge voltage. The strongest emissions come from oxygen and nitrogen in the air which occupy the longer wavelength side of the spectrum [15]. At the shorter wavelength side, the atomic lines of copper are clear and stronger than those from the air. This result indicates that the spark discharge has enough power to strip and excite atoms which provide possibility for elemental imaging analysis.

### 3.2. Selection of discharge voltage

Overall, the discharge can be divided into three stages: the light emission begins from about 1200 V without sounding (corona discharge at this stage) and without atomic lines; the second stage is spark discharge (starting from about 1650 V) with visible spark and clear sounding; and when discharge voltage is beyond 3050 V, the discharge produces massive light (Fig. 3b), with noise, heat and significant frequency increasing, causing serious damage of the sample

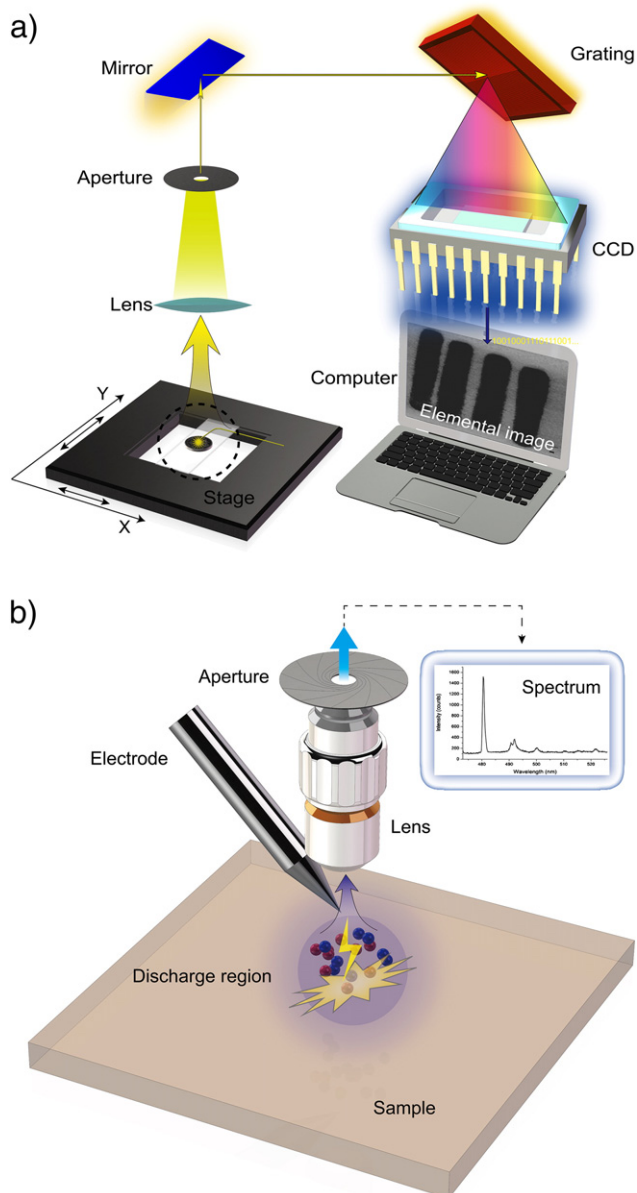


Fig. 1. (a) The experimental setup of the imaging system; and (b) schematic diagram of optical emission process.

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